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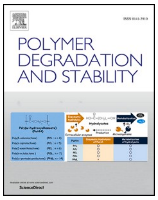

Biomass-derived poly(lactic acid) and poly(3-methyl-1,5-pentanediol sebacate) alternating multiblock copolymers with improved marine biodegradability and mechanical properties

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ABSTRACT

The reliance on fossil resources and the mismanagement of waste owing to the rapid increase in plastic production have led to serious environmental problems, particularly global marine pollution. In recent years, poly (lactic acid) (PLA) has been widely used as a biomass plastic to replace petroleum-based materials. However, the biodegradation of PLA is limited to composting environments and its brittle nature limits its application. This study aimed to synthesize a biomass-based PLA and poly(3-methyl-1,5-pentanediol sebacic acid) (PMPDSe)-diol copolymer and evaluate its marine biodegradability and mechanical properties. PLA was copolymerized with PMPDSe-diol to obtain the triblock copolymer PLA-PMPDSe-PLA, which was then chain-extended with hexamethylene diisocyanate to form an alternating multiblock (PLA-*alt*-PMPDSe) copolymer. Because of their regular arrangement, the thermal and mechanical properties could be controlled by varying the length of the PLA chains, compared with random multiblock (PLA-*ran*-PMPDSe) copolymers. In particular, when 61 % or 71 % PLA was included, the films had higher elongation at break (331 %–518 %) and toughness than PLA and PLA-*ran*-PMPDSe copolymers. Biodegradability was the highest when 54 % PLA was used, and the films disintegrated in compost and seawater. In seawater, the molecular weight decreased to 45 % in three months, and the biodegradability was confirmed to be >17 % in two months. Furthermore, the PLA-*alt*-PMPDSe copolymer exhibited a contact angle of over 83°, which is equivalent to that of PLA and could be used as a film. This polymer has a wide range of applications and will contribute to the development of sustainable bioplastics and address plastic waste.

1. Introduction

Plastics have become an indispensable part of our lives, and their production has grown rapidly since 1950, reaching 460 million tons (Mt) in 2019 [1]. However, the dependence on fossil resources [2,3] and the mismanagement of plastic disposal [4] have caused serious environmental problems. In the 1980s, the use of fossil resources reached a critical level, necessitating a gradual reduction of these resources in industrial applications [3]. Since then, attention has shifted to sustainable bioresources, and bioplastic production is projected to increase to 7.43 Mt by 2028 [5]. Marine pollution caused by plastics, which has been reported since the early 1970s, is a global problem [6,7]. It is estimated that 11.6 Mt of improperly managed plastics will be discharged into aquatic environments by 2060, of which 4 Mt will be discharged into the ocean [1]. Discarded fishing gear can seriously impact marine organisms [8,9], and microplastics can accumulate throughout the food chain and affect human health [10,11]. Therefore, it is essential to develop biodegradable plastics from sustainable bioresources. Poly (lactic acid) (PLA) is an attractive bio-based and biodegradable material with desirable properties such as ease of manufacture, zero toxicity, biocompatibility, high mechanical strength, thermoplasticity, and compostability [12–14]. Thus, PLA is a major candidate for industrial applications, accounting for 31 % of bioplastic production at 0.68 Mt in 2023, and is expected to grow to 43.6 % or 3.24 Mt in the next five years [5]. It is ultimately decomposed into H_2O and CO_2 [13,15], hydrolyzed into low-molecular-weight oligomers in the compost, and mineralized by microorganisms [15,16]. However, the biodegradation of PLA is limited to composting environments [17,18], and it is poorly biodegradable in seawater owing to the lack of microorganisms [19]. This is because the glass transition temperature (T_g) of PLA is higher than ambient temperature, which prevents its conversion to a lower molecular weight [13,17]. Owing to the presence of complicated and

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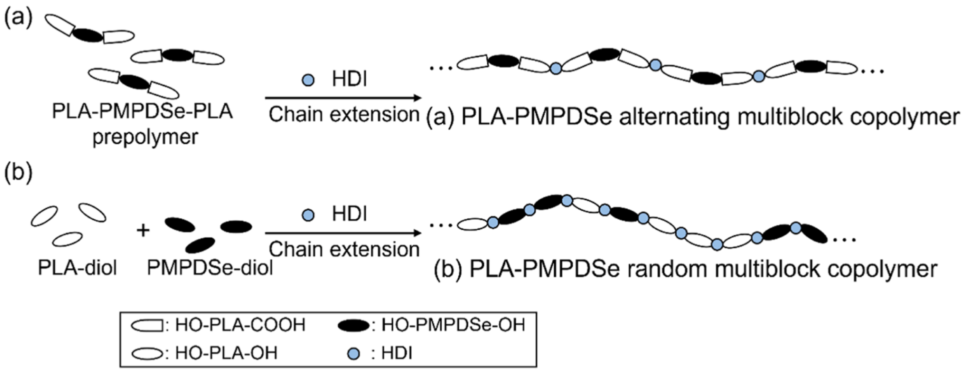

Fig. 1. Model structures of (a) PLA-*alt*-PMPDSe and (b) PLA-*ran*-PMPDSe copolymerization. The OH group side of the segment is shown rounded and the COOH group side is shown flat.

uncontrollable external factors, researchers have focused on the intrinsic degradation factors of polymers in marine environments, such as their crystallinity, T_g, and hydrophobicity [20,21]. Recently, PLA oligomers have been reported to exhibit potential marine biodegradability in marine environments [22], and the possibility of microorganisms suggesting marine biodegradation of PLA chains in marine environments has also been mentioned [23,24]. Melt blending or copolymerization with biodegradable materials is a practical approach for improving the potential marine biodegradability of PLA. Blends with water-soluble, degradable thermoplastic starch [25] or polyvinyl alcohol [26] take advantage of the readily degradable nature of the material, with the biodegradable domains being degraded primarily by the incorporated material, whereas PLA itself remains stable. Furthermore, inspired by the intramolecular transesterification mechanism of ribonucleic acid (RNA), which rapidly hydrolyzes due to its phosphate ester linkages, an attempt has been made to improve degradability in seawater by introducing synthetic phosphate linkages as breaking points into PLA through copolymerization [27]. The introduction of biodegradable units into PLA through copolymerization also compensates for the brittleness of PLA [14,24]. Copolyesters with long-chain dicarboxylic acids introduced into the polyethylene succinate and polybutylene succinate backbones exhibit high marine biodegradability [28]. Therefore, we hypothesized that the introduction of long-chain dicarboxylic acids into PLA-based polymers would generate numerous degradation points and improve their marine biodegradability. Sebacic acid is produced by the alkaline pyrolysis of castor oil [29] and has attracted attention as a raw material for bioplastics [30], and promising results have been obtained in biodegradation tests of polymers based on it [31,32]. Poly (3-methyl-1,5-pentanediol sebacate) diol (PMPDSe-diol), which uses sebacic acid as the dicarboxylic acid and 3-methyl-1,5-pentanediol (MPD) as the diol, was developed by Kuraray Co., Ltd. [33]. Currently, MPD is made from petroleum, but Kuraray Co., Ltd. is already producing partially bio-based products in some of its plants certified under the ISCC PLUS sustainable product certification system [34]. Other studies have been conducted to convert MPD into fully bio-based products [35,36], and Visolis Inc. is developing bio-based products [37,38]. To the best of our knowledge, the synthesis and evaluation of the versatility and biodegradability of PLA-based copolymers using sebacic acid as the biodegradable unit have not been extensively discussed. For example, studies related to synthesis have reported the formation of relatively low molecular weight PLA-(poly(sebacic acid)) PSA triblock copolymers, which have been investigated for their degradation and drug release properties in drug delivery applications [39,40]. Additionally, Poly(alditol sebacate)-PLA copolymers have been synthesized and studied for their wettability and hydrolytic degradation properties in water [41]. Compared to these studies, we focus on the synthesis and evaluation of high molecular weight PLA-based copolymers using sebacic acid units as the biodegradable unit, aiming to control the mechanical properties and improve biodegradability.

In this study, PLA-based PLA-PMPDSe alternating multiblock (PLA-*alt*-PMPDSe) copolymers were synthesized via the copolymerization of PLA and sebacic acid-based prepolymers, followed by a chain extension reaction with hexamethylene diisocyanate (HDI). Copolymers with different PLA chain lengths were prepared via ring-opening polymerization. Regularly arranged PLA-*alt*-PMPDSe copolymer (a) films were compared to PLA-PMPDse random multiblock (PLA-*ran*-PMPDSe) copolymer (b) films and their thermal and mechanical properties and biodegradability were evaluated (Fig. 1). To contribute to the development of sustainable bioplastics with high biomass content materials, this study aimed to control the thermal and mechanical properties of PLA by changing its chain length, as well as to improve the biodegradability of the copolymers.

2. Materials and methods

2.1. Materials

PMPDSe-diol ($M_n = 2000$) (Kuraray Polyol P-2050) was supplied by Kuraray Co., Ltd. (Tokyo, Japan). Chloroform was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Tin (II) 2-ethylhexanoate, methanol, diethyl ether, sea sand (425–850 μm), ammonium chloride and soda lime were purchased from Fujifilm Wako Pure Chemical Co. (Osaka, Japan). L-lactide, 1,4-butanediol, HDI, and potassium dihydrogen phosphate were purchased from Tokyo Chem. Inc. (Tokyo, Japan). PLA (Ingeo™ Biopolymer 2003D) was purchased from Nature Works LLC (Nebraska, USA). All the reagents were used as received.

2.2. Synthesis of PLA-PMPDSe alternating multiblock (PLA-alt-PMPDse) copolymers

To synthesize PLA-PMPDSe-PLA, PMPDSe-diol and L-lactide were placed in a 50-mL three-neck flask and vacuum-dried at room temperature for 3 h. To synthesize copolymers with different PLA chain lengths, the amount of L-lactide was adjusted, with ratios of PMPDSe-diol/ L-lactide = 5 g/5 g, 3 g/6 g, 2 g/8 g, or 1 g/8 g. A solution of tin(II) 2-ethylhexanoate (1.0 mol% of the hydroxyl end of the PMPDSe-diol) was added to the mixture, which was then vacuum dried at room temperature for 2 h. The ring-opening polymerization was performed at 180 °C for 3 h with stirring (150 rpm) under a nitrogen atmosphere. Subsequently, HDI was added to the mixture at a NCO/OH molar ratio of 1.5 mol^{-1}. The chain-extension reaction proceeded at 180 °C for 0.5 h with stirring (100 rpm) under a nitrogen atmosphere. The final product was dissolved in chloroform and poured into excess methanol for reprecipitation. The precipitate was filtered, washed with methanol, and dried under vacuum to obtain PLA-*alt*-PMPDSe copolymers as white solids.

2.3. Synthesis of PLA-PMPDSe random multiblock (PLA-ran-PMPDSe) copolymers

The PLA-diol was synthesized by the ring-opening polymerization of L-lactide, using 1,4-butanediol as the initiator, as described in Section 2.2. To synthesize PLA-diol with different PLA chain lengths, the amount of L-lactide was adjusted, with ratios of 1,4-butanediol/ L -lactide = 0.63 g/14 g, 0.45 g/20 g, 0.23 g/20 g, or 0.11 g/20 g. The synthesized mixture was dissolved in chloroform and poured into excess diethyl ether for reprecipitation. The precipitate was filtered, washed with diethyl ether, and dried under vacuum to obtain PLA-diol. To synthesize the PLA-*ran*-PMPDSe copolymers, PLA-diol with different chain lengths and PMPDSe-diol were placed in a flask in equimolar amounts, and HDI was added at an NCO/OH molar ratio of 1.5 mol^{-1}. The mixture was then heated at 180 °C for 0.5 h with stirring (100 rpm) under a nitrogen atmosphere. The final product was dissolved in chloroform and poured into excess methanol for reprecipitation. To obtain the PLA-*ran*-PMPDSe copolymers, the precipitate was filtered, washed with methanol, and dried under vacuum. For comparison, chain-extended PLA (PLA-CE) was prepared by placing PLA-diol in a flask, adding HDI at an NCO/OH molar ratio of 1.5 mol^{-1}, and heating at 180 °C for 0.5 h with stirring under a nitrogen atmosphere. Similarly, PMPDSe-CE was prepared by adding PMPDSe-diol and HDI at an NCO/OH molar ratio of 1.5 mol^{-1}, and heating under the same conditions as PLA-CE. Reprecipitation for both PLA-CE and PMPDSe-CE was performed using chloroform and methanol.

2.4. Fabrication of films

To examine their mechanical properties, the prepared samples were heated and compressed using a manual hydraulic heating press (IMC-180C, Imoto Mfg. Co., Ltd., Kyoto, Japan) to produce the films. The sample (5 g) was sandwiched between aluminum plates set with 0.5 mm spacers. The press was then heated to a temperature above the melting point for 5 min. The sample was melted and held at 20 MPa for 10 min to produce a film of 70.0 × 70.0 × 0.5 mm^3. To investigate the degradability characteristics, the sample (3 g) was sandwiched between aluminum plates set with 0.1 mm spacers. The press was then heated to a temperature above the melting point for 5 min. The sample was melted and held at 20 MPa for 10 min to produce a film of 70.0 × 70.0 × 0.1 mm^3.

2.5. Measurement

The molecular structure of the sample was analyzed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy using chloroform-d as a solvent with a JNM-ECS400 (400 MHz) (JEOL Ltd., Tokyo, Japan). The molecular weights of the products were determined using size exclusion chromatography (SEC) (HLC-8420GPC EcoSEC-Elite, Tosoh Co., Yamaguchi, Japan) with a refractive index detector and a TSKgel GMH_{HR} column (Tosoh Co., Yamaguchi, Japan). The SEC test was performed at a flow rate of 1.0 mL/min at 40 °C using chloroform as the eluent, which was calibrated using polystyrene standards ($M_n = 1.31 \times 10^3 - 3.64 \times 10^6$). The mechanical properties of the prepared samples were determined via tensile testing using an Auto Graph Table-TOP universal testing machine (AGS-X, Shimadzu Co., Kyoto, Japan) at a cross-head speed of 10 mm/min. T_g and melting temperatures (T_m) of the samples were measured by differential scanning calorimetry (DSC) using a thermal analysis system using a DSC6220 (Hitachi High-Tech Science Co., Tokyo, Japan). The sample (approximately 3 mg) were prepared (drying conditions: dried overnight at 90 °C, then slowly cooled) was heated from −80 to 200 °C at a heating rate of 10 °C/min, and then kept at 200 °C for 3 min to melt. After the heating, the sample was cooled from 200 to −80 °C at a cooling rate of 10 °C / min. The temperature was maintained at −80 °C for 3 min. The sample was heated again from −80 to 200 °C at a heating rate of 10 °C/min. DSC measurements were performed under a nitrogen atmosphere at a flow rate of 50 mL/min. The crystallinity of PLA blocks in the copolymer was calculated as follows:

$$X_c\ (\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_0 \times f_{PLA}} \times 100,$$

where X_c is crystallinity, f_{PLA} is the weight fraction of PLA block in copolymer, ΔH_m is exothermic enthalpy, ΔH_{cc} is the endothermic enthalpy of cold in reheating scan, and ΔH_0 is the theoretical melting enthalpy of the 100 % crystalline PLA homopolymers, equal to 93 J/g [42]. Thermal degradation temperature (T_d) of the sample was measured by thermogravimetric analysis (TGA) with a thermal analysis system using a NEXTA STA200RV (Hitachi High-Tech Science Co., Tokyo, Japan). The samples (approximately 5 mg) were placed in a Pt pan and heated from 50 to 500 °C under N_2 atmosphere at a heating rate of 10 °C/min. Films were prepared (drying conditions: dried overnight at 90 °C, then slowly cooled) and X-ray diffractometer (XRD) analysis for films was carried out using an XRD (RINT-Ultima, Rigaku Co., Ltd., Tokyo, Japan) operated at 45 kV and 200 mA. Data were collected within the range of scattering angles (2θ) of 5° to 50° at the rate of 5 °/min. Water contact angle (WCA) tests were conducted to evaluate the durability of the samples, WCA test was carried out. In the WCA test, the hydrophobicity of the film was evaluated from contact angle measurements of water droplets deposited on the film surface using a goniometer Drop Master DM300 (Kyowa Interface Science Co. Ltd., Saitama, Japan) equipped with a charge coupled device (CCD) camera. The acquired images were analyzed using FAMAS software ver. 2.3.1 (Kyowa Interface Science Co., Ltd., Saitama, Japan).

2.6. Disintegration test of films with compost

Films buried in the compost YK-12 from Yawata Bussan Co. were set in a constant-temperature and constant-humidity chamber KCL-2000A (EYELA Co., Ltd., Tokyo, Japan) and evaluated visually and by measuring the weight of the recoverable films. Table S1 summarizes the analytical values of compost YK-12 purchased from Yawata Bussan Co. Following Japanese Industrial Standard (JIS) K6953–2:2010) after the addition of dried sea sand (320 g) to the compost (dry mass of 60 g), the moisture content was adjusted to approximately 58 %, and left for eight weeks at the test temperature of 58 °C and constant humidity. Square films of 4 cm^2 were used in the test. To prevent film scattering, the films were sandwiched between a larger nylon mesh (mesh size of 125) and crimped with Polysealer P-200 (Fuji Impulse Co., Ltd., Osaka, Japan).

2.7. Biodegradation test and disintegration test of films in seawater

The biodegradability of the film in seawater was evaluated according to ASTMD6691–17 using a RESPIROMETRIC Sensor System 6 for Plastic Biodegradability (VELP Scientifica S.r.l., Usmate, Italy) [43]. This technique quantifies the aerobic biodegradation capacity of organic matter by measuring the biochemical oxygen demand (BOD), which indicates the amount of oxygen consumed by microorganisms. Soda lime (1 g) containing sodium hydroxide was placed at the top of a sealed bottle as a CO_2 absorbent. The sealed bottle was then placed in an incubator maintained at 30 °C and stirred continuously in the dark for 2 months. The RESPIROMETRIC Sensor transmits data directly to a PC, allowing real-time monitoring of the analysis curve. The seawater used in the BOD test was collected from Odaiba, Tokyo Bay, on a rainy evening of July 17, 2024. The collected seawater was filtered through a 77 μm mesh filter, and conditions were adjusted by adding inorganic salts to achieve concentrations of 0.5 g/L of ammonium chloride and 0.1 g/L of potassium dihydrogen phosphate. Biodegradation tests were conducted under aerobic conditions at 30 °C for two months. The film samples (approximately 0.5 cm) were cut into small pieces, placed in 250 mL of test seawater, and stirred at 180 rpm. The C, H, and N contents

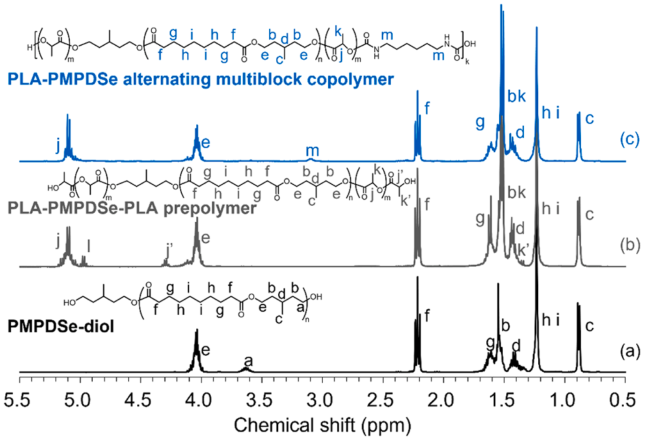

Fig. 2. ^{1}H NMR spectra of (a)PMPDSe-diol, (b) PLA-PMPSe-PLA and (c) PLA-*alt*-PMPDSe copolymers.

(%) of the samples were analyzed in the CHN measurement mode using an organic element analyzer Vario EL Cube (Elementar Ltd., Hanau, Germany). The O content was calculated by subtracting the C, H, and N contents from the total contents (Table S2). The results were used to calculate the theoretical oxygen demand (ThOD) of the sample. As a blank, a BOD test was performed using seawater without any added sample. The biodegradability of each film was calculated as follows:

$$\text{Biodegradability (\%)} = \frac{(\text{BOD (mg/L) of the sample} - \text{BOD (mg/L) of the blank}) \times \text{Test seawater volume (L)}}{\text{ThOD (mg/mg)} \times \text{Sample (mg)}} \times 100$$

For the disintegration test in seawater, seawater was collected on the morning of August 9, 2024, from Odaiba, Tokyo Bay, on a clear day, and adjusted in the same manner as mentioned above. Square films of size 2 cm and 250 mL of the adjusted seawater were placed in a 500 mL bottle and shaken at 30 °C and 150 rpm for three months using a Bio-Shaker BR-3000 L shaking incubator (Taitech Co., Saitama, Japan). To investigate the amount of microorganisms in the seawater, biofilms attached to the films were suspended in the test seawater used for the three month disintegration test. Samples (100 mL) were aliquoted and filtered through mixed cellulose esters membrane with pore size of 0.65 μm (Merck Millipore Inc., MA, USA) and polycarbonate track-etched membranes with pore size of 0.2 μm (it4ip S.A., Louvain-la-Neuve, Belgium). Total deoxyribonucleic acid (DNA) was extracted from both filters using ISOIL for Beads Beating kit (Nippon Gene Co., Toyama, Japan) and DNeasy PowerClean Pro Cleanup Kit (Qiagen Inc., Hilden, Germany) and analyzed for DNA concentration and A260/A280 in seawater using spectrophotometer NanoDrop ND8000 (Thermo Fisher Scientific Inc., MA, USA). The collected samples were assessed for weight change and visually inspected.

3. Results and discussion

3.1. *Synthesis of PLA-PMPDSe alternating multiblock (PLA-alt-PMPDSe) copolymers*

PLA-PMPDSe-PLA triblock copolymers were synthesized by the ring-opening polymerization of L-lactide using PMPDSe-diol as an initiator. PLA-*alt*-PMPDSe copolymers were synthesized via a chain-extension reaction. Fig. 2 shows the representative ^{1}H NMR spectra. The CH_2 signal of the terminal group of the PMPDSe-diol was detected at 3.6 ppm (a), indicating that it was terminated with a hydroxyl group (Fig. 2a). The PLA-PMPDSe-PLA triblock copolymer with the ring-opening polymerization of PMPDSe-diol showed typical PLA and PMPDSe signals (Fig. 2b). The CH_3 and CH signals of the lactate repeating unit appeared as two strong signal peaks at 5.1 (j) and 1.5 (k) ppm, respectively. The CH_2 signal attributed to the sebacic acid unit of the PMPDSe chain was assigned to 2.2 (f), 1.6 (g), 1.2 (h, i) ppm, the CH_3 signal attributed to the MPD unit to 0.9 (c) ppm, the CH_2 signal to 4.0 (e), 1.5 (b), and the CH signal to 1.4 (d). The CH and CH_3 signals of the PLA chain end groups are

Table 1
Synthesis of the prepolymer by ring-opening polymerization and chain-extension reaction with HDI.

	Ring-opening polymerization [a]						Chain-extension [b]				
	PLA [c] (%)	Oligomer [d] (theo.) (Da)	Lactide conversion (%)	M_n PLA [e] (NMR) (Da)	M_n Total [e] (NMR) (Da)	Yield (%)	[NCO]/[OH] [f] (mol/mol)	M_n [g] (SEC) (Da)	M_w [g] (SEC) (Da)	M_w/M_n [g]	Yield (%)
PMPD-CE	0	2000	–	–	–	–	1.5	20000	37000	1.9	65
PLA-*alt*-PMPDSe	54	4000	95	3600	6700	49	1.5	60000	180000	3.0	95
	61	6000	95	4800	7900	55	1.5	53000	130000	2.5	94
	71	10000	96	7100	10000	80	1.5	59000	140000	2.4	93
	85	18000	98	15000	17700	83	1.5	48000	120000	2.5	96
PLA-*ran*-PMPDSe	59	2000	96	3000	–	59	1.5	35000	96000	2.7	79
	68	4000	95	4200	–	78	1.5	29000	69000	2.4	95
	79	8000	97	7400	–	85	1.5	32000	60000	1.9	94
	89	16000	98	16900	–	90	1.5	45000	92000	2.0	97
PLA-CE	100	8000	97	7400	–	85	1.5	41000	76000	1.9	95

[a] At 180 °C for 3 h.
[b] At 180 °C for 0.5 h.
[c] PLA-*alt*-PMPDSe copolymer: PLA (%) = PLA (determined by ^{1}H NMR)/overall (determined by ^{1}H NMR) × 100.
PLA-*ran*-PMPDSe copolymer: Preparation ratio of diols and HDI.
[d] Theoretical molecular weight of PLA synthesized by lactide ring-opening polymerization.
[e] Determined by ^{1}H NMR.
[f] Preparation ratio of HDI and diols.
[g] Determined by SEC (in chloroform).

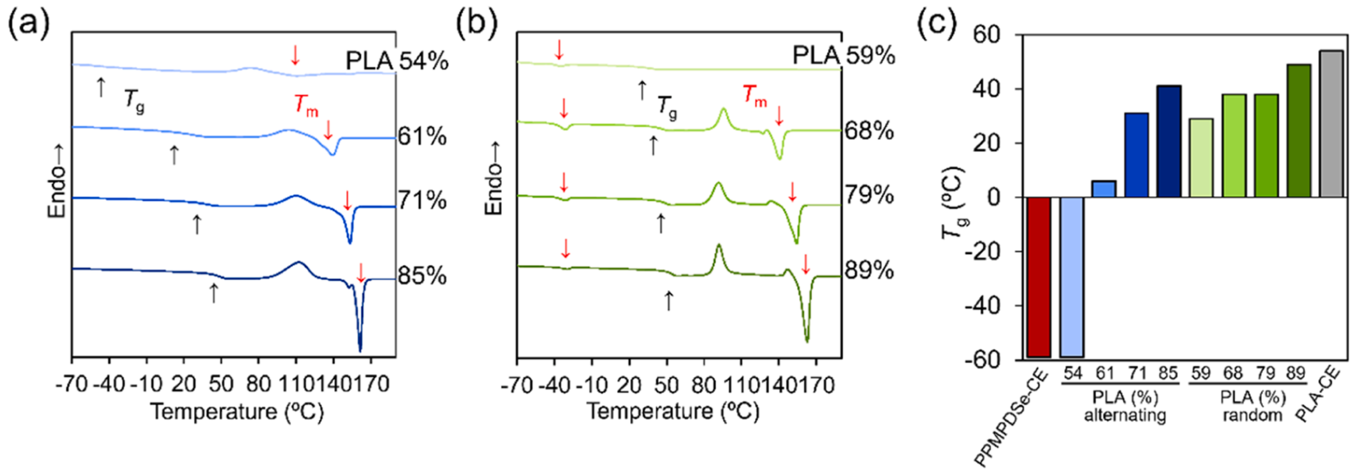

Fig. 3. Thermal parameters of each sample. (a) Second heating curves of DSC of PLA-*alt*-PMPDSe copolymers, (b) PLA-*ran*-PMPDSe copolymers, and (c) T_g of each sample.

Table 2
Thermal parameters of each sample by DSC. The degree of X_c of each sample determined by XRD.

		DSC				XRD
	PLA (%)	T_g (°C)[a]	T_m (°C)[a]		X_c (%)[b]	X_c (%)[c]
PMPDSe-CE	0	−59	−30		–	
PLA-*alt*-PMPDSe	54	−59	111		27	24.4
	61	6	139		33	36.6
	71	31	153		33	39.4
	85	41	162		41	43.3
PLA-*ran*-PMPDSe	59	29	−35	–	26	28.7
	68	38	−32	140	31	33.1
	79	38	−32	154	37	38.6
	89	49	−30	160	37	42.6
PLA-CE	100	54	156		31	43.8
Neat PLA	100	55	152		30	45.5

[a] Determined by DSC.
[b] Degree of crystallinity of PLA from DSC was calculated.
[c] Degree of crystallinity from XRD was calculated.

detected at 4.3 ppm (j') and 1.4 ppm (k'), indicating that the triblock prepolymer is terminated with a hydroxyl group. The lactide conversion (%) in the ring-opening polymerization reaction was calculated using the integral ratio of the PLA-derived signal (5.1 ppm (l)) to the lactide-derived signal (5.0 ppm (j)), as shown in Fig. 2b. The lactide conversion reached >95 % in all samples, indicating successful ring-opening polymerization. Typical signals of the PLA and PMPDSe chains in the PLA-*alt*-PMPDSe copolymer are shown in Fig. 2c. The CH_2OCONH signal adjacent to the urethane bond is assigned to 3.1 ppm (m), and the signals at the lactate terminus corresponding to 4.3 ppm (j') is infinitesimally small, indicating that the terminal hydroxyl group of the triblock prepolymer reacted with the isocyanate. Table 1 summarizes the synthesis of the copolymers. The molecular weight of the PLA chain was determined by ^{1}H NMR from the ratio of the 5.1 ppm integral value (j) attributed to the lactate repeating unit to the 4.3 ppm integral value (j') of the lactate terminus. In addition, the molecular weight of the PMPDSe chain was determined by ^{1}H NMR using the ratio of the 4.3 ppm integral value (j') attributed to the repeating unit to the 4.0 ppm integral value (e) of the lactate terminus. The molecular weight of the entire PLA-PMPDSe-PLA triblock copolymer was calculated by summing the

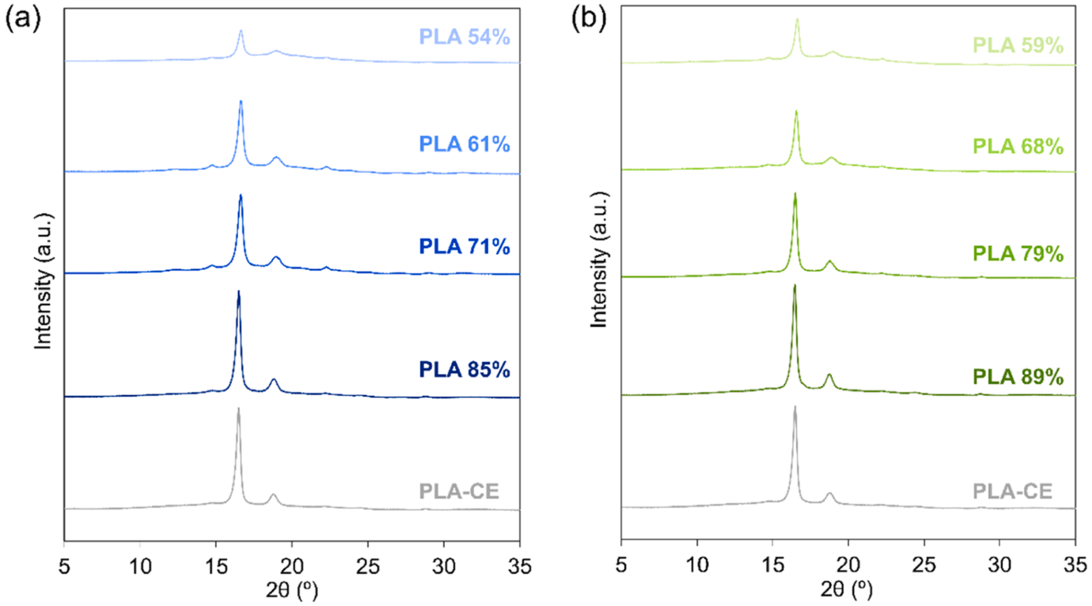

Fig. 4. XRD patterns of (a) PLA-*alt*-PMPDSe and (b) PLA-*ran*-PMPDSe copolymers.

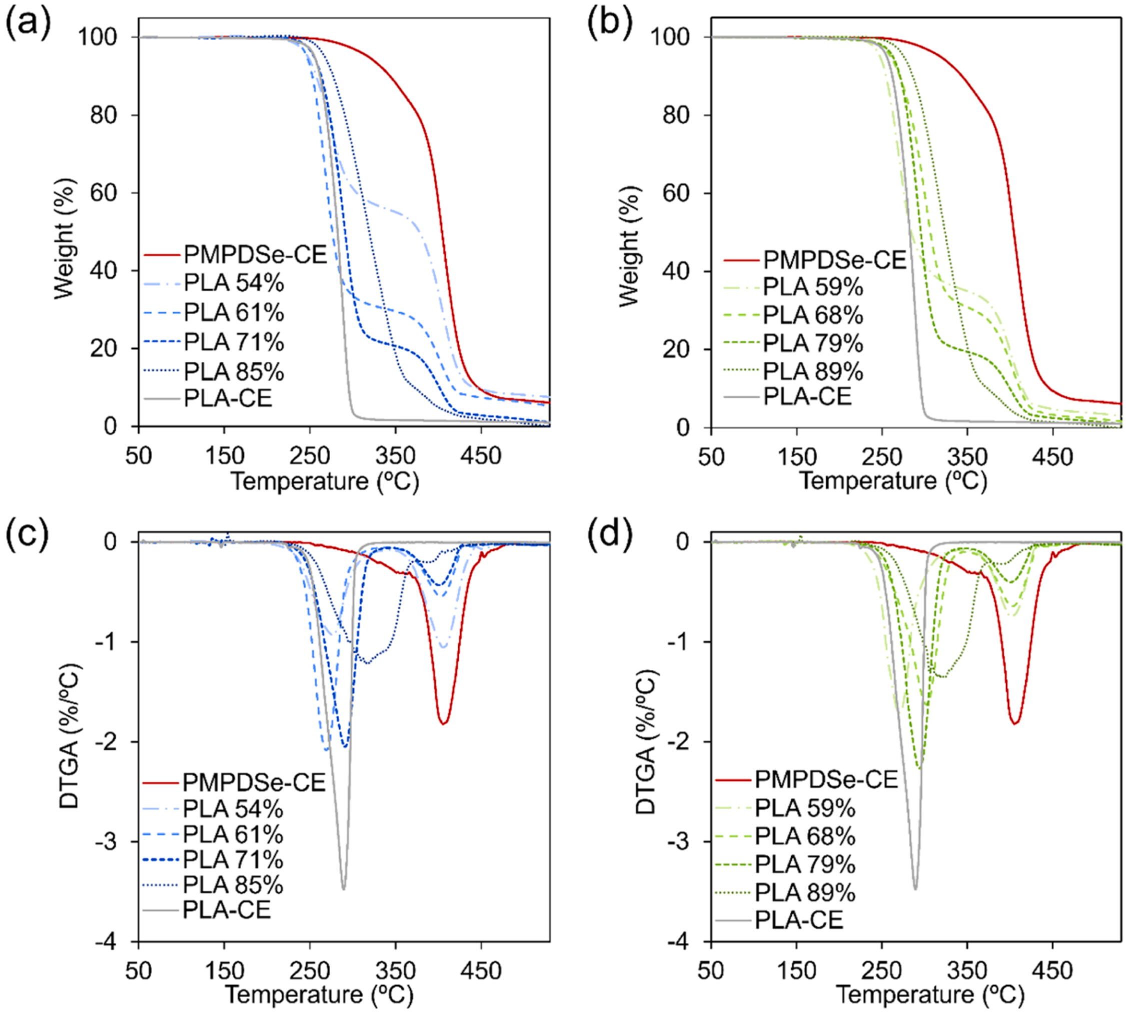

Fig. 5. Thermal parameters of each sample. (a) TGA curves of PLA-*alt*-PMPDSe and (b) PLA-*ran*-PMPDSe copolymers. (c) DTGA curves of PLA-*alt*-PMPDSe and (d) P PLA-*ran*-PMPDSe copolymers.

molecular weights of PLA and PMPDSe using ^{1}H NMR. PLA (%) was calculated from the molecular weight of the entire PLA-PMPDSe-PLA triblock copolymer and the PLA chain. Triblock copolymers with PLA chains of different lengths (M_n = 3600, 4800, 7100, and 1500) were synthesized by adjusting the stocking ratios of L-lactide. Then, HDI was added at NCO/OH molar ratio of 1.5 mol^{-1} to synthesize PLA-*alt*-PMPDSe copolymers (Table 1). The ^{1}H NMR spcetra of the PLA-*ran*-PMPDSe copolymers is shown in Figure S1. To match the PLA composition with the PLA-*alt*-PMPDSe copolymer, PLA-diol (M_n = 3000, 4200, 7400, and 16900) was synthesized by changing the L-lactide stock ratio, after which HDI was added to PLA-diol and PMPDSe-diol to synthesize PLA-*ran*-PMPDSe copolymers (Table 1).

3.2. *Thermal parameters of each sample*

Fig. 3 shows the evaluation results of the thermal properties obtained using DSC. The DSC curve of the PLA-*alt*-PMPDSe copolymer exhibited a single T_m because the crystallinity of the PMPDSe chains sandwiched in the triblock structure by the PLA chains was suppressed [44]. T_m and T_g increased with increasing PLA content and decreased with decreasing PLA content (Fig. 3a). In the PLA-*ran*-PMPDSe copolymers, the PMPDSe and PLA chains were irregularly arranged, presumably resulting in the crystallinity of each block and multiple melting transitions (Fig. 3b). Similar behavior was observed for other PLA-based thermoplastic polyurethanes [44–46]. In the case of the PLA-*ran*-PMPDSe copolymers containing 61 %, the crystallinity of the PLA chains was suppressed because of the short PLA chain length, probably because of the PMPDSe chains, with a single T_m. The DSC results for the PLA-*alt*-PMPDSe copolymer, PLA-*ran*-PMPDSe copolymer, PLA-CE, PMPDSe-CE, and neat PLA are summarized in Table 2. The DSC curves for the PLA-CE and PMPDSe are shown in Figure S2. Both the PLA-*alt*-PMPDSe and PLA-*ran*-PMPDSe copolymers exhibited a single T_g and were miscible between blocks in the amorphous region [24,47]. The copolymers showed lower T_g values than neat PLA and PLA-CE, suggesting the effect of the introduction of PMPDSe chains (Fig. 3c). In particular, in the case of PLA-*alt*-PMPDSe copolymer, the units of the triblock structure are regularly arranged, and it is assumed that the soft segments increase the overall mobility of the polymer, resulting in a significant decrease in T_g. It has also been reported that the regular structure due to alternating multiblock leads to more flexible polymer chains and consequently lower T_g values [24,44]. On the other hand, the PLA-*ran*-PMPDSe copolymers are assumed to have restricted molecular motion due to the irregular and localized arrangement of the rigid PLA units. The presence of these rigid units constrains the overall mobility of the polymer chains, leading to higher T_g values. This is also correlated with the mechanical properties (Table 4). Figure S3 presents the first heating of DSC of the heat-treated film. The introduction of PMPDSe chains disrupted the alignment of the PLA chains [48], resulting in higher crystallinity of the PLA-*alt*-PMPDSe and PLA-*ran*-PMPDSe copolymers with longer PLA chains (Table 2). The X_c value calculated from the XRD pattern was

Table 3
Thermal parameters of each sample by TGA. Thermal degradation parameters of polymers in terms of the onset degradation temperature at a mass loss of 5 wt% ($T_{d,\ 5\ \%}$), maximum degradation rate (peak) temperature ($T_{d,\ max}$).

	PLA (%)	Thermal properties (TGA) $T_{d,\ 5\ \%}$ (°C)	$T_{d,\ max\ PLA}$ (°C)	$T_{d,\ max\ PMPDSe}$ (°C)
PMPDSe-CE	0	318	–	404
PLA-*alt*-PMPDSe	54	248	276	405
	61	246	269	403
	71	255	292	402
	85	267	319	392
PLA-*ran*-PMPDSe	59	247	270	402
	68	260	301	403
	79	262	295	401
	89	275	321	393
PLA-CE	100	255	302	–
Neat PLA	100	328	367	–

higher than that calculated from the DSC test (Table 2); however, these values cannot be directly compared because the two calculation methods are completely different. Fig. 4a and b show the XRD patterns of the copolymers recorded after isothermal crystallization. PLA-CE has the typical diffraction peaks of PLA at 2θ = 14.8° (010), 16.6° (200/110), 18.9° (203), and 22.2° (210). In all the copolymers, the PLA chains were long enough to form crystalline phases and had diffraction peaks. While 2θ = 16.6° is known as a strong peak, 2θ = 22.2° is generally reported as a weak peak for PLA [45]. The copolymerization further weakened the PLA peaks, but the peak at 2θ = 22.2° was still slightly observed. Previous studies have shown that polyurethanes containing branched-chain structures, such as MPD, often exhibit amorphous properties [49] and may have low crystallinity owing to hindered molecular packing. These copolymers showed no differences in the diffraction peak positions depending on the copolymerization method or composition and exhibited characteristics of semi-crystalline polymers similar to the characteristic crystal structure of PLA. Both the PLA-*alt*-PMPDSe and PLA-*ran*-PMPDSe copolymer showed a decreasing trend in the intensity of the corresponding peaks with decreasing PLA chain length and crystallinity (Table 2).

3.3. Thermal stabilities of each sample

The thermal stability of the PLA-PMPDSe multiblock copolymers under nitrogen atmosphere was evaluated using TGA. The TGA curves of the PLA-*alt*-PMPDSe and PLA-*ran*-PMPDSe copolymers are shown in Fig. 5a and b, respectively, and their respective DTGA curves are shown in Fig. 5c and d. Data such as temperature at 5 % weight loss ($T_{d,\ 5\ \%}$) and maximum decomposition temperature ($T_{d,\ max}$) are shown in Table 4. Nearly no residue remained after thermal degradation. Taking the degradation onset as starting at a temperature corresponding to $T_{d,\ 5\ \%}$, neat PLA showed a degradation onset at 328 °C, with $T_{d,\ max}$ located at 367 °C, which is not significantly different from previous studies [50, 51]. Compared to neat PLA, PLA-CE showed a lower thermal degradation temperature due to the shorter PLA chains, with a degradation initiation temperature of 255 °C and a $T_{d,\ max}$ of 302 °C, again not significantly different from previous studies [52] (Table 3). In contrast to simple homopolymers, the copolymers exhibited a two-step thermal degradation, with the PLA chains degrading in the first step, followed by the degradation of the introduced PMPDSe chains. All copolymers were thermally stable up to 246 °C, with $T_{d,\ max}$ above 269 °C. There was a decrease in $T_{d,\ max\ PLA}$ for copolymers with a lower PLA content owing to shorter PLA chains. In contrast, the thermal degradation temperature of the PMPDse chains in the copolymer was similar to that of PMPDSe-CE and remained stable and unaffected by the presence of PLA. The thermal degradation temperature of the PLA-*ran*-PMPDSe copolymer is slightly higher than that of the PLA-*alt*-PMPDSe copolymer, probably because of the longer PLA chains in the former.

Table 4
Mechanical properties of polymers.

	PLA (%)	Mechanical properties (tensile test) Young's modulus (MPa)	Maximum stress (MPa)	Elongation at break (%)	Toughness (MJ/m^3)
PLA-*alt*-PMPDSe	54	110 ± 16	4.7 ± 0.3	200 ± 35	7.0 ± 0.6
	61	504 ± 11	19.4 ± 1.2	518 ± 31	49.3 ± 0.2
	71	1520 ± 130	28.2 ± 3.1	331 ± 23	65.7 ± 5.7
	89	2540 ± 75	46.3 ± 3.2	5.90 ± 1.9	1.80 ± 0.50
PLA-*ran*-PMPDSe	59	472 ± 21	8.43 ± 0.45	130 ± 10	7.20 ± 0.72
	68	1290 ± 61	21.5 ± 0.8	2.9 ± 0.4	0.32 ± 0.01
	79	1910 ± 67	24.8 ± 1.3	2.33 ± 0.45	0.26 ± 0.03
	89	2440 ± 110	40.5 ± 5.9	11.6 ± 7.0	3.02 ± 1.83
PLA-CE	100	2830 ± 110	52.6 ± 1.8	2.83 ± 0.21	1.00 ± 0.01
Neat PLA	100	2880 ± 30	49.9 ± 3.2	2.26 ± 0.09	0.61 ± 0.06

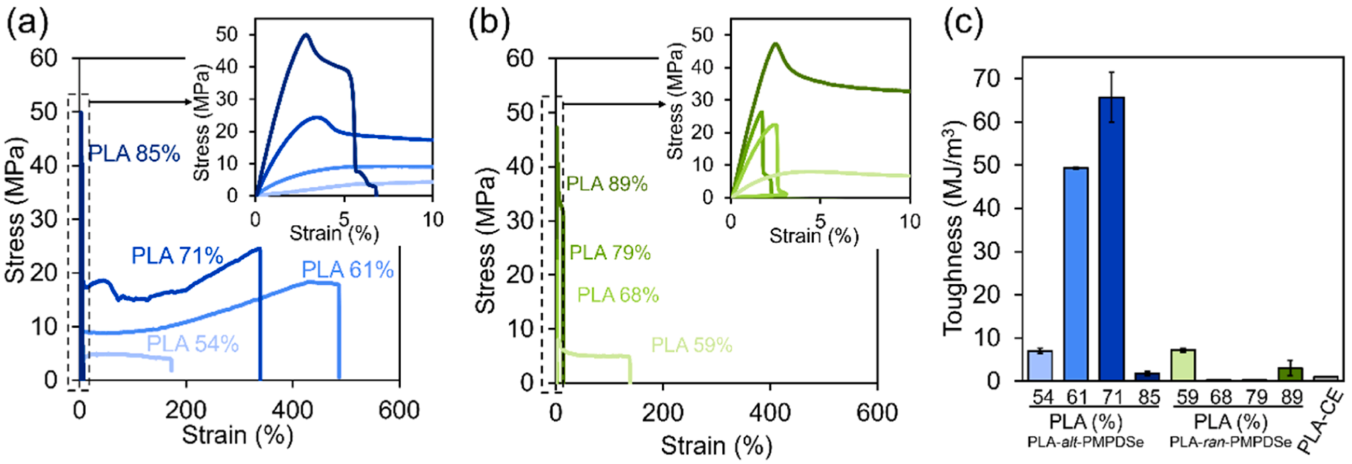

Fig. 6. Stress–strain curves obtained by tensile tests of hot-pressed films of (a) PLA-*alt*-PMPDSe and (c) PLA-*ran*-PMPDSe copolymers. (c) Toughness obtained by a tensile test (average, three replicates).

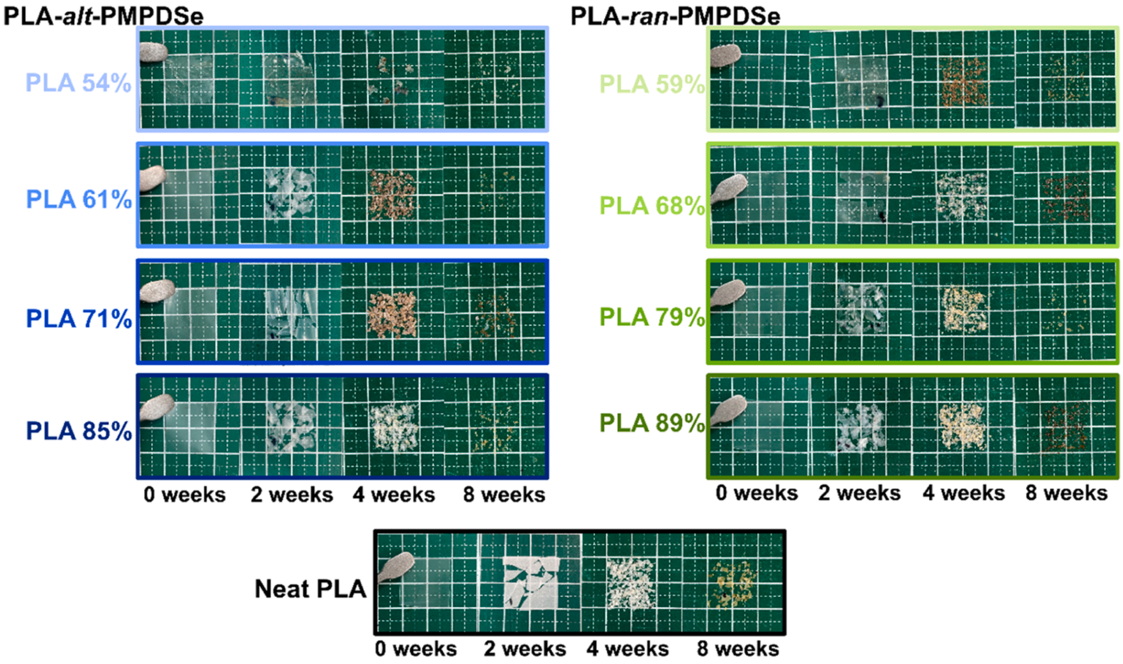

Fig. 7. Disintegration tests of PLA-*alt*-PMPDSe copolymer, PLA-*ran*-PMPDSe copolymer and neat PLA film in compost for eight weeks.

3.4. Mechanical properties of hot-pressed films

As shown in Fig. 6, the mechanical properties of the hot-pressed films were evaluated using tensile tests. Fig. 6a shows the stress-strain curves of PLA-*alt*-PMPDSe copolymers containing 54–85 % PLA, and Fig. 6b shows the stress-strain curves of PLA-*ran*-PMPDSe copolymers containing 59 %–89 % PLA. Fig. 6c compares the toughness of the PLA-*alt*-PMPDSe copolymers with that of the PLA-*ran*-PMPDSe copolymers and PLA-CE. Table 4 presents the results of the tensile tests. As shown in DSC curves in Figure S2, PMPDSe-CE has low T_m and is oil-like at room temperature, making film formation impossible. As shown in the XRD results, the crystallinity increased with an increasing number of PLA chains (Fig. 4), and the tensile strength of the PLA-*alt*-PMPDSe copolymer increased and became comparable to that of PLA-CE. In contrast, the elongation at break increased with a decrease in the PLA chain content, which was attributed to the influence of the soft segment and a decrease in crystallinity. The PLA-*alt*-PMPDSe copolymers containing 61 % and 71 % PLA maintained higher elongation at break and tensile strength and showed higher toughness than the PLA-*ran*-PMPDSe copolymers. Previous studies have also reported that a regular continuous structure, owing to its high molecular weight and chain extension, contributes to high toughness [53]. These results suggest that even with small amounts of PMPDSe chains, regularly arranged PLA-*alt*-PMPDSe copolymers have excellent mechanical properties. Furthermore, this suggests that the tensile properties can be adjusted by controlling the composition, making it a highly versatile material.

3.5. Disintegration test in compost and biodegradation test in activated sludge

Fig. 7 shows a simple appearance test of PLA-*alt*-PMPDSe copolymer, PLA-*ran*-PMPDSe copolymer, and neat PLA films buried in compost to determine whether the film decomposed in eight weeks. Two weeks after the test began, all tested films became brittle and began to tear, although no significant weight changes were observed (Figure S4). After four weeks, all films had become more finely fragmented, and samples with relatively lower PLA contents lost more weight. In contrast, neat PLA and samples with higher PLA contents maintained their weight. After eight weeks, many samples were infinitesimally fine and were expected to disappear completely with further extension of the study period. In particular, the copolymers showed a more pronounced weight loss than PLA, suggesting that degradation occurred more rapidly than in neat PLA because of the active microbial environment and high temperature and humidity of the compost. Previous studies have reported that PLA not only loses weight in compost [23,52] but also biodegrades completely, and we assume that PLA and copolymers will biodegrade in compost as well in this test. The PLA-*alt*-PMPDSe copolymer containing 54 % PLA, which showed significant disintegration in compost, BOD, and biodegradation in activated sludge compared to neat PLA, is shown in Figure S5a and b (Supporting experimental section S1). After 28 d of incubation, the copolymer was biodegradable (12 %), but the neat PLA did not begin to degrade. The biodegradability of the copolymer tended to increase after 28 d, and it is assumed that biodegradability will increase further with longer testing periods. This is assumed to be due to the low T_g of the PLA-*alt*-PMPDSe copolymers. In compost and activated sludge, the polymer chains become more flexible, accelerating hydrolysis and microbial attachment. Lower T_g and crystallinity make the amorphous regions of polymer chains more flexible, allowing more water to penetrate the interchain spaces and facilitating hydrolysis and microbial degradation [13,15–17]. The introduction of long-chain dicarboxylic acids into non-marine biodegradable plastics has been reported by Kumagai et al. to improve biodegradability; however, crystallinity and glass transition temperature may not be the only influences and may have a role yet to be fully understood [28]. Further assessment of biodegradability and hydrophobicity in seawater was pursued, as we explored the possible influence of factors specific to long-chain dicarboxylic acids.

3.6. Marine biodegradation and disintegration test

Fig. 8 shows how PLA-*alt*-PMPDSe and PLA-*ran*-PMPDSe copolymers disintegrate or biodegrade in seawater compared to PLA. Fig. 8a shows the change in film appearance in seawater for a PLA-*alt*-PMPDSe copolymers containing 54 % PLA and a PLA-*ran*-PMPDSe copolymer containing 59 % PLA. The neat PLA film maintained its shape for three months in seawater, but the PLA-*alt*-PMPDSe copolymer containing 54 % PLA showed coloration, presumably due to microbial biofilms, and the film changed shape and lost 15.3 % of its weight in three months.

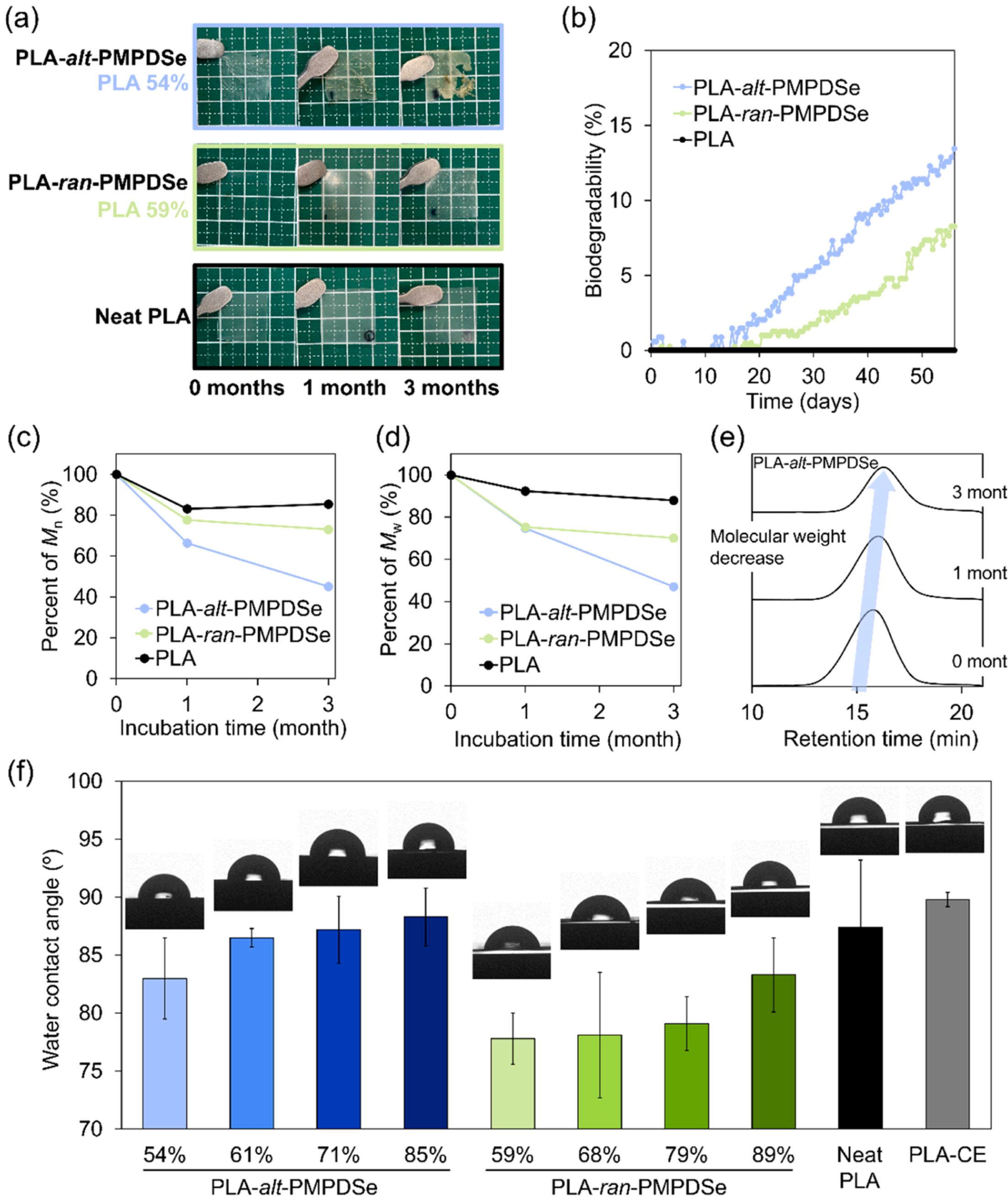

Fig. 8. Marine biodegradation and disintegration tests of PLA-*alt*-PMPDSe copolymer containing 54 % PLA, PLA-*ran*-PMPDSe copolymer containing 59 % PLA and neat PLA. (a) Change in film appearance in seawater for threee months. (b) Biodegradability of films cut into small pieces for two months. Biodegradability was calculated using ThOD determined from the CHNO content (Table S2). (c) M_n (%) and (d) M_w change (%) of films in seawater over three months. (e) Molecular weight shifts of PLA-*alt*-PMPDSe copolymer containing 54 % PLA by SEC. (f) WCA of each film of copolymers and PLA.

The weight of the PLA-*ran*-PMPDSe copolymer containing 59 % PLA decreased by 0.5 %. Figure S6 shows the samples of all films assessed for disintegration in seawater, including the sample shown in Fig. 8a, which did not change significantly in appearance. Fig. 8b shows the biodegradability of the PLA-*alt*-PMPDSe copolymer containing 54 % PLA, the PLA-*ran*-PMPDSe copolymer containing 59 % PLA, and neat PLA. We selected the PLA-*alt*-PMPDSe copolymer containing 54 % PLA and the PLA-*ran*-PMPDSe copolymer containing 59 % PLA based on the significant weight loss observed in the compost degradation test (Figure S4). Additionally, weight loss in seawater was observed in both samples (Fig. 8a and Figure S6). Consistent with the results of the disintegration test shown in Fig. 8a, neat PLA showed almost no increase in biodegradation for two months, whereas the copolymer showed an increase in BOD, indicating oxygen consumption by microorganisms (Figure S7). The biodegradability was 8.3 % for the PLA-*ran*-PMPDSe copolymer and 17.2 % for the PLA-*alt*-PMPDSe copolymer. It is known that the microbial concentration in seawater is lower compared to soil, compost, and freshwater [17,19]. The amount of DNA in the blank seawater was low, but the amount of DNA increased significantly when measured after the disintegration test. PLA-*alt*-PMPDSe copolymers showed more than a twofold increase in DNA content compared to neat PLA and PLA-*ran*-PMPDSe copolymers, confirming the increase in microbial content (Table S3). This suggested that the PLA-*alt*-PMPDSe copolymer formed a unique microbial community called the “plastosphere” that was distinct from the surrounding seawater [54–57]. It was assumed that the activation and growth of microorganisms was enhanced, making the polymers more easily biodegradable. Fig. 8c and d show the molecular weight changes measured by SEC. The molecular weight of the PLA-*alt*-PMPDSe copolymer began to decrease from the beginning of the test, and after three months decreased from $M_n = 20300$, $M_w = 48800$ to $M_n = 9100$, $M_w = 23000$, a significant decrease to 45.1 % of the initial M_n value. The molecular weight of PLA decreased from $M_n = 53300$, $M_w = 121000$ to $M_n = 45600$, $M_w = 106000$ but maintained 85.4 % of the initial M_n value. The molecular weight of the PLA-*ran*-PMPDSe copolymers decreased from $M_n = 27400$, $M_w = 133000$ to $M_n = 20000$, $M_w = 93300$, but maintained 70.2 % of the initial M_n value. Fig. 8e shows the change in the molecular weight distribution curve of the PLA-*alt*-PMPDSe copolymer tested for three months. The SEC curve showed no significant change in the polydispersion but a peak shift from the high-molecular-weight side to the low-molecular-weight side. Figure S8 shows the SEC curves for PLA and PLA-*ran*-PMPDSe copolymers; no significant peak shifts were observed. Compared to neat PLA, multiblock copolymers have a lower T_g and crystallinity (Table 2), which may have reduced their molecular weight and facilitated biodegradation in seawater, similar to what occurs in compost and activated sludge. In the PLA-*ran*-PMPDSe copolymer, the PMPDSe and PLA chains were arranged irregularly; however, in the PLA-*alt*-PMPDSe copolymer, the PMPDSe chains were arranged regularly between the PLA chains, which may affect the efficiency of hydrolysis and the possibility of a low molecular weight [23]. For PLA to biodegrade, several bonds need to be cleaved in the initial stages of degradation, reducing to oligomer sizes that can be metabolized by microorganisms [16,22]. In this study, it was also assumed that the degradation of copolymer to low molecular weight in seawater affected its biodegradability. Although there are few reports on the evaluation of the biodegradability of polyester polyurethanes such as PLA-*alt*-PMPDSe copolymers in marine environments, degradation has been reported to occur [24,58], and microbial degradation has also been reported to occur under aerobic conditions in soil and compost [23,58–62]. In this study, biodegradability was evaluated in simulated compost, activated sludge, and marine environments, but further enzymatic degradation experiments and field tests in natural environments are needed. Furthermore, when the WCA of the films were measured (Fig. 8f), the contact angle tended to decrease as the number of PMPDSe chains containing sebacic acid increased; however, no penetration of water droplets was observed, suggesting that the film was fully functional. The contact angle of PLA was 89.8 ± 0.6°, whereas that of the PLA-*alt*-PMPDSe copolymer was 83.0 ± 3.5° and that of the PLA-*ran*-PMPDSe copolymer was 77.8 ± 2.2°. The slight decrease in hydrophobicity may also be a factor in improved hydrolysis and biodegradability. Although this improvement in marine biodegradability could not be fully elucidated, it is assumed to be due not only to the crystallinity, hydrophobicity, and hydrolyzability of the polymers examined in this study, but also to various factors, such as enzyme affinity due to the presence of sebacic acid, a long-chain dicarboxylic acid, as reported in previous studies [28].

4. Conclusion

To improve the brittleness and biodegradability of PLA, PLA-*alt*-PMPDSe copolymers were synthesized from biomass-derived PLA and PMPDSe containing sebacic acid as a structural unit. Compared with PLA-*ran*-PMPDSe copolymers, the thermal and mechanical properties of the resulting copolymers can be easily controlled by simply changing the length of the PLA chains. The PLA-*alt*-PMPDSe copolymers containing 61 % or 71 % PLA had significantly higher elongation at break and toughness than the PLA and PLA-*ran*-PMPDSe copolymers, suggesting that the regularly arranged PMPDSe chains improved functionality. Biodegradability was highest when the PLA-*alt*-PMPDSe copolymers containing 54 % PLA, and the film disintegrated in compost and seawater. Initial biodegradation was also observed in activated sludge. Even in seawater, the regular arrangement of PMPDSe chains between PLA chains promoted oligomerization, resulting in a biodegradation rate of over 17 % in two months. In the WCA test, the water droplets did not penetrate immediately and the contact angle of the PLA-*alt*-PMPDSe copolymers was comparable to that of neat PLA (>83°), suggesting that it functioned well as a film. The improved biodegradability may be due not only to the crystallinity, hydrophobicity, and hydrolyzability of the polymer, but also to the long-chain dicarboxylic acid, sebacic acid; however, further research is needed to explore the possibility of complete mineralization. This research is expected to be deployed in a variety of applications requiring high toughness and biodegradability such as packaging, agricultural applications, and marine environments.

CRediT authorship contribution statement

Atsuki Takagi: Writing – original draft, Methodology, Investigation, Conceptualization. **Yu-I Hsu:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Hiroshi Uyama:** Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2025.111301.

Data availability

No data was used for the research described in the article.

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