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락타이드-엡실론데카락톤 공중합체 계층형 마이크로셀룰러 구조 바이오 폼의 광대역 흡음 성능 구현에 대한 연구

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락타이드-엡실론데카락톤 공중합체

계층형 마이크로셀룰러 구조 바이오 폼의 광대역 흡음 성능 구현에 대한 연구

지도교수 곽 승 엽

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서울대학교 대학원

재료공학부

박 희 영

박희영의 공학석사 학위논문을 인준함

2023 년 7 월

위 원 장	안 철 희	(인)
부위원장	곽 승 엽	(인)
위 원	도 준 상	(인)

Abstract

Fabrication of a poly(L-lactide-*co*-E-decalactone) bio-foam with hierarchical microcellular structure for broadband sound absorption

Heeyoung Park

Department of Materials Science and Engineering

The Graduate School

Seoul National University

In order to improve the low-mid frequency acoustic absorption properties of porous sound absorption materials, it is known that the formation of a hierarchical pore structure as well as the excellent damping properties of the material itself are the critical factors that should be considered. Herein, we present a complementary design for copolymeric bio-foam, poly(L-lactide-coε-decalactone) (PLDL), through a statistical copolymerization and subsequent thermally-induced phase separation (TIPS) with lyophilization. This endows the final copolymeric bio-foam material with both major and minor pores ranging from hundreds of micrometers to tens of nanometers. The PLDL biofoam with hierarchical microcellular structure possess the more tortuous propagation paths, showing the improvement of the low-mid sound absorption performance. Moreover, the incorporation of amorphous and flexible εdecalactone (*\varepsilon*-DL) enables the PLDL to exhibit improved noise damping ability, resulting in the remarkable enhancement of sound absorption coefficient in a broad range of frequencies. Notably, the prepared PLDL biofoam with a half the thickness of commercial PU foam shows almost analogous acoustic absorption capability over the entire frequency range. Our present work may be expected to contribute to the ongoing efforts regarding the design and fabrication of high-performance sustainable sound absorption materials.

Keywords

Poly(L-lactide); Poly(ε-decalactone); Statistical copolymerization; Thermally-induced phase separation (TIPs); Lyophilization; Hierarchical microcellular structure; Bio-foam; Viscoelastic property; Broadband acoustic absorption

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1. Introduction

Noise pollution has been perceived as a serious problem in recent centuries, due to the fast development of industries and transportation. [1]. Especially, transportation vehicle has noise sources both structure-borne and air-borne noise pollution. [2]. Continuous exposure to noise pollution can cause several disadvantages, such as psychiatric problems like fatigue and hypertension, as well as physical illnesses [3],[4],[5].

Accordingly, various kinds of sound absorption materials have gained enormous attention. Currently, commercial sound absorption materials in vehicles can be divided into two categories: acoustic panels and porous sound absorption materials [6],[7]. The panel absorber (e.g. Helmholtz resonators and perforated panels) exhibited good sound attenuation in low frequencies owing to internal resonance and transmission loss effect.[8] Nevertheless, because the panels reflect most of the acoustic energy except for the resonance frequency, most acoustic panels have narrow acoustic absorption frequency range that may restrict their applicability.[9] These sound absorbers exhibit good performances in low frequencies (< 1600 Hz). In contrast to acoustic panels, porous acoustic absorption materials, such as melamine foam (MF),[10] polyurethane (PU) foam, **[11]** fiber-based materials, [12] show a relatively broad acoustic absorption frequency spectrum and have advantages of facile material fabrication and processing. However, polymer foams as sound absorbers often show poor sound absorption in low-mid range frequencies [13] [14]. Although the acoustic absorption properties at low frequency ranges can be improved by increasing the mass density of the materials [15], there are limitations in application to industrial fields that require lightweight materials. Thus, it is crucial to design a lightweight porous acoustic absorption material with enhanced acoustic absorption capability in low-mid frequency ranges.

Manipulation of microstructure is considered one of the significant approaches for affecting sound absorption performance. [16] Especially, it is known that the formation of hierarchical microcellular structure including multiscale pore size distribution can provide tortuous sound wave pathways and larger contact area between sound wave and pore wall, resulting in the enhancement of sound attenuation in low-mid frequency. [17-20] Previously, various researches to realize hierarchical microcellular pore structure have been attempted, including particulate leaching[20], impregnation[21], electrospinning[17, 22], freeze drying method[19], and phase separation[23, 24] and etc. NINE, Md Julker, et al. reported that the sound absorption performance of melamine foam further improved at 500 - 4000 Hz result from hierarchical pore structure through dipping melamine foams in graphene oxide dispersion (GO). [21] Cao, Leitao, et al. reported that the interweaved polyacrylonitrile-cellulose nanocrystal composite aerogel exhibited excellent sound absorption performance in low-mid frequency and robust mechanical property attributed to high tortuosity based on maze-like structure.[17]

Among these methods, designing the hierarchical microcellular pore structure via the phase separation and freeze-drying technique is considered as an effective and convenient method. For example, Fotsing, Edith Roland, et al. reported the acoustic characteristics of Poly(lactic acid) (PLA) foam fabricated by nonsolvent-induced phase separation (NIPS). The foams have meso/microporous hierarchical structure and showed better sound absorption performance than only mesoporous foam. However, the poor interconnectivity of pores resulted in narrow sound absorption band at low frequency.[23] Therefore, to achieve excellent sound absorption in broadband frequencies with phase separation method, further approach might be needed for preparation well-interconnected hierarchical porous material.

Meanwhile, the viscoelastic properties of the porous acoustic absorption materials are another controlling factors affecting the sound absorption capability. It has been widely reported that the control of viscoelastic damping of the porous acoustic absorption materials via chemical modification such as copolymerization[11, 25] blending polymers[26], and incorporation of crosslinker [27] have a great impact on improving sound absorption performance. Litauszki, Katalin, and Ákos Kmetty. et al. previously reported that blending polymers which have different physical properties could enhance the material acoustic damping ability. The viscoelastic property of poly(lactide) and poly(butylene succinate) blends was optimized with controlling weight ratios of those polymers. However, this research primarily focused on material damping and did not specifically address the manipulation of micro porous structure [28]. To the best of our knowledge, there is few reports presenting research design for achieving broadband sound absorption materials simultaneously considering formation of hierarchical porous structure and improvement intrinsic viscoelastic property of polymer material. Furthermore, due to the trend of developing environmentally sustainable materials and reducing dependence on petroleum-based polymers, there is a growing interest in using bio-derived polymers as acoustic absorption materials, replacing PU and other commercial foams. [12, 29, 30] Therefore, in order to develop lightweight green porous acoustic absorption materials in the future, it is essential to optimize the viscoelastic damping properties and design biopolymers with a hierarchical microcellular structure.

Polylactide (PLA) has gained attention among the bio-derived polymers because it is one of the most commercialized polymers and has excellent mechanical properties that are compatible with other commercial polymers such as poly(ethylene terephthalate) (PET), and polystyrene (PS). PLA has a high damping factor, which is closely related to vibration-damping performance [31][33]. Therefore, PLA foams have been widely studied and considered in various acoustic absorption materials [20, 23, 28, 32, 33]. However, PLA has intrinsic brittleness, resulting in low toughness and limited practical applications [34-36]. To improve these limitations of PLA, introducing flexibility is widely approached. Poly(ε -decalactone) (PDL) is a bio-derived polymer like PLA, but it possesses excellent flexibility due to its amorphous structure. With a low glass transition temperature of around – 60°

C, PDL exhibits a rubbery consistency at room temperature, making it highly promising for industrial applications [37-39]. By copolymerizing PLA with PDL, the mechanical properties of PLA can be easily modified [40, 41]. One commonly employed method to synthesize these copolymers and obtain controlled microstructures is ring-opening bulk polymerization.

In this study, we developed a complementary design for copolymeric biofoam, poly(L-lactide-*co*-ɛ-decalactone) (PLDL), through a statistical copolymerization and subsequent thermally-induced phase separation (TIPS) with lyophilization. The chemical and physical properties, microcellular structures, viscoelastic properties, and acoustic absorption properties of the prepared PLDL bio-foams were comprehensively analyzed. To investigate viscoelastic damping characteristic of PLDL series in a wide frequency range $(0.1 - 10^6 \text{ Hz})$, the time-temperature superposition (TTS) method was implemented using DMA results. It was observed that the design strategies endow the resulting copolymeric bio-foam material with multimodal pore structure consisting of hundreds of micrometers to tens of nanometers cells. The PLDL bio-foam with hierarchical microcellular structure possess the more tortuous propagation paths, showing the improvement of the low-mid sound absorption performance. Moreover, the incorporation of ~30 mol% amorphous ε -decalactone (ε -DL) enables the PLDL foam (i.e., PLDL70) to exhibit excellent noise damping ability in wide audio frequency range, resulting in the remarkable enhancement of sound absorption coefficient in a broad range of frequencies.

2. Experimental

2.1. Materials

L-(-)-Lactide (>98.0%) was supplied by Tokyo Chemical Industry, Japan. ϵ -decalactone (>99%), tin(II) 2-ethyl hexanoate (Sn(Oct)₂; 92.5–100%), diethylene glycol (99%) 1,4-dioxane (99%) and chloroform-d (99.8%) obtained from Sigma-Aldrich, Ltd., Korea. Chloroform (extra pure grade) and Methanol (extra pure grade,) were purchased from Daejung Chemicals. All chemicals were used as received, without further purification.

2.2. Synthesis of Poly(L-lactide-co-ε-decalactone) (PLDLs)

Poly(L-lactide-co- ε -decalactone) (PLDL) series were synthesized via one pot-one step ring-opening bulk polymerization (ROP) of L-lactide (LLA) and ε -dacalactone(ε -DL) with Sn(Oct)₂. L-lactide and ε -decalactone were dried at reduced pressure for at least 48 h prior to use. The procedure used for the synthesis of PLDLs was as followed: LLA and ε -DL were added to a threeneck, round-bottom flask (100ml) under a nitrogen atmosphere. The polymerizations were conducted using increasing molar ratios of LLA: ε -DL, from 100:0 to 70:30; a control experiment using neat ε -DL yielded PDL for comparison with the new copolymers. The monomer(s) and initiator; [M]/[I] $\approx 300-400$) mixtures were added to the flask and immersed into a controlled temperature oil bath (150 °C) with vigorous stirring. After forming a homogeneous phase, a catalytic amount of Sn(Oct)₂ ([M]/Sn(Oct)₂ \approx 200) was added to the flask, and the ROP was performed for 20h. The resulting PLDL copolymers were cooled to room temperature, and the products were dissolved in chloroform and precipitated in excess of cold methanol. The precipitated products were dried under reduced pressure at 60 °C for 24 h.



Figure 1. Schematic illustrations of synthesis of PLDL via ring-opening polymerization in one pot process.

Sample code	Target molar ratio		
	PLLA	PεDL	
PLLA	100	0	
PLDL90	90	10	
PLDL80	80	20	
PLDL70	70	30	

Table 1. Sample code and the composition of PLDL for preparing foams.

2.3. Fabrication of PLDL hierarchical microcellular foams

Thermally-induced phase separation (TIPS) was used to produce Poly(1lactide-co-ɛ-decalactone) (PLDL) foams. For preparing the foams, the homogeneous polymer solutions were cooled until phase separation occurred, and then the solvent was removed to achieve porous structures. In this study, PLDLs were dissolved in 1,4-dioxane at a concentration of 5% (w/v). This was achieved by heating and stirring the mixture until a clear, homogeneous polymer solution was obtained at approximately 70°C. The polymer solutions were poured into a cylindrical glass container. The containers were sealed and immediately cooled at -20°C. During the cooling process, phase separation occurred, leading to the formation of a porous structure within the solution. After the phase separation process, the samples were allowed to rest for 24 hours. The samples were subjected to lyophilization for 48 hours using a freeze-dryer (TFD8501, IlshinBiobase). Lyophilization, also known as freezedrying, involves the removal of solvent from the sample under vacuum conditions. The lyophilization process was carried out in a freeze-dryer with a pressure maintained below 100 mTorr and a condenser temperature set at -90°C. These conditions ensured efficient removal of the solvent while maintaining the integrity of the foams.

Fabrication of PLDL Foam (TIPS process)



Figure 2. Schematic illustration of the fabrication of PLDL hierarchical foams by thermally-induced phase

separation (TIPS) and lyophilization.

2.4. General characterization

2.4.1 Characterization of PLA and PLDL Copolymers

Attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectra were measured in the range $4000-600 \text{ cm}^{-1}$ (Thermo-Fisher Scientific, Waltham, MA).

The proton nuclear magnetic resonance at 600MHz (¹H NMR; Avance 600, Bruker) spectra was recorded in a Chloroform-d₆ solvent to identify the chemical structure and composition of the prepared PLDLs.

Thermogravimetric analysis (TGA; Discovery TGA 5500, TA Instruments) was conducted at the heating rate of 10 °C/min under an N₂ atmosphere. Differential scanning calorimetry (DSC; Discovery DSC25, TA Instruments) was performed. The samples were first heated to 200 °C to remove thermal history, cooled to -80 °C, and then second heated to 200 °C. The experimental were set to 10 °C/min for each step and set under N₂ atmosphere. The crystallinity index (χ_c) of the PLDL series was calculated using the following equation (1).

$$\chi_c[\%] = \left(\frac{\Delta H_m}{\Delta H_{theo}}\right) \times 100 \tag{1}$$

 ΔH_m is the melting enthalpy (J/g) estimated from the melting peak in the DSC

curve, and ΔH_{theo} is the enthalpy of 100% crystalline PLA (93.7 J/g) [41].

X-ray diffraction (XRD; New D8 Advance, Bruker) were collected over a 2θ range of 5-40 ° at room temperature with a scan rate of 2° min⁻¹.

2.4.2 Characterization of PLDL foams and pore morphology

The porosity of the PLDL foams was obtained by measurement and calculated with equation (2).

$$P[\%] = 100 (1 - D_{foam}/D_{polymer})$$
 (2)

 D_{foam} is the obtained bulk density of PLDL foams calculated from the weight and volume of the foam. The D_{polymer} is the density of the obtained PLDL copolymers.

Field-emission scanning electron microscopy (FESEM; SIGMA, Carl Zeiss) was analyzed The SEM was operated at an accelerating voltage of 10 kV. In order to prepare the samples, the cryogenic fracture surface was securely mounted using carbon tape. The surface of the samples was further coated with a thin layer of platinum using a sputter coating technique.

Mercury intrusion porosimetry (MIP; Autopore V 9620, Micromeritics) was conducted. The foam samples were first evacuated to a pressure of 50 μ m Hg for 5 minutes. Subsequently, the samples were allowed to reach equilibrium for 10 seconds under initial Hg pressure and were then scanned within a pressure range of 0.51 to 17400 psi (380 μ m-0.01 μ m).

¹H NMR cryoporometry (NMR; mini spec mq20) analysis was used for determining nanometer-scale cells. The samples were dried for 24h at reduced

pressure and immersed in cyclohexane for at least 24 h. After removing excess liquid on the surface of the samples, the samples were completely frozen at 200 K. In the experiment, a spin-echo pulse sequence $(90^{\circ}-\tau-180^{\circ}-\tau-echo)$ was employed with a 90° pulse length of 2 µs and a pulse separation time of 10 ms. The recycle delay, T, was set to a value greater than 5 times the relaxation time. The temperature was increased stepwise by 4 K up to 230 K, then in 1 K steps from 230 K to 270 K, then in 0.5K steps from 270 K to 280 K using a temperature control unit (Bruker BVT-3000) with ± 0.1K precision. The measured signals were recorded in thermal equilibrium, achieved by a stabilization time of 600 s. The signal intensity obtained from the measurements was corrected with Curie's law and the PSD was calculated for each foam sample.

2.5. Performance evaluation

2.5.1 Dynamic mechanical property

Dynamic mechanical analysis was performed on rectangular specimens with dimensions of $5 \times 20 \text{ mm}^2$ and a thickness of about 0.3 mm. The analysis was carried out in tension mode at a frequency of 1 Hz, with the temperature ranging from -30 to 90 °C and a heating rate of 3 °C min⁻¹. Under an N₂ atmosphere, the specimens were subjected to an oscillatory strain of 10 µm. The apparent activation energy (E_a) was obtained from the loss tangent (tan δ) peaks observed in the multifrequency mode (at applied frequencies of 1, 2, 5, 10, and 15 Hz) during the heating process. The following Arrhenius relationship (3) demonstrates the relationships between applied frequency and the apparent activation energy

$$\log f = \log A - E_a/2.303R(1/T)$$
 (3)

f represents the measured frequency, R is the gas constant, T is the experimental temperature, and A is the frequency factor. The apparent activation energy (E_a), to measure the chain mobilities of PLDLs, was determined by calculating the slope of the log f plotted against 1000/T and fitting the data linearly. To assess the energy damping characteristics over a frequency range of 1 Hz to 100 Hz at a temperature of 25 °C, frequency sweeps

were performed with 10 measurement intervals per decade. Additionally, a master curve was constructed by conducting frequency sweeps at five different isothermal temperatures: 10 °C, 15 °C, 20 °C, 25 °C, and 30 °C This allowed for the extension of the test frequency range using the Time-temperature superposition (TTS) method.

2.5.2 Sound absorption performance of PLDL foams

The sound absorption coefficient (SAC) of the foam samples was measured using a two-fixed microphone impedance tube (4206-T, Bruel & Kjaer) in accordance with ASTM E1050. The measurement was conducted within a frequency range of 100 to 6400 Hz. The experimental setup involved connecting the sound source to one end of the impedance tube, while the foam specimen with a diameter of 29 mm was mounted on the other end. The impedance tube allowed for the precise measurement of sound absorption properties. The acoustic absorbing capacity of the foam samples was evaluated using two parameters: the noise reduction coefficient (NRC) and the average sound absorption coefficient. The acoustic absorbing capacity of All samples in terms of noise reduction coefficient (NRC) and average sound absorption coefficient, given by Equation.

NRC =
$$\frac{a_{250} + a_{500} + a_{1000} + a_{2000}}{4}$$
 (4)

Avg. SAC =
$$\frac{a_{125} + a_{250} + a_{500} + a_{1000} + a_{2000} + a_{4000}}{6}$$
 (5)

where α_{125} α_{250} , α_{500} , α_{1000} , and α_{2000} are the acoustic absorption coefficients at the frequency of 125, 250, 500, 1000, and 2000 Hz, respectively. The NRC provides an overall measure of sound absorption performance, especially in low-mid frequencies. The average sound absorption coefficient provides an assessment of sound absorption across a broader range of frequencies including the lower and higher frequencies than NRC.



Figure 3. Experimental setup for the measurement of the sound coefficient.

3. Results and Discussion

3.1. Synthesis and characterization of PLLA-PDL copolymers

3.1.1. Analysis of chemical structure

ATR FT-IR spectroscopy was utilized to analyze the chemical structures of the PLDL series. The obtained FT-IR spectra of PLLA, PLDL, and a reference PDL are depicted in Fig. 4. In all samples, a pronounced carbonyl (C=O) stretching band was observed at 1724 cm⁻¹, indicating the presence of ester groups. In the PLDLs, additional peaks at 2862 cm⁻¹ and 2932 cm⁻¹ were observed, which correspond to the symmetric and asymmetric stretching vibrations of methylene (C-H) groups in the PDL moieties. These peaks were not present in neat PLLA, suggesting that they originated from the PDL component of the copolymers. The intensity of these PDL-related peaks increased with a higher proportion of PDL in the PLDLs, indicating an increased molar ratio of PDL. These results verified that the PLDL copolymers were qualitatively synthesized.

The ¹H analyses were performed to investigate the PLLA and PDL conversions, the incorporation of the initiators, and the chemical composition of the prepared PLDL. In the ¹H NMR spectra in Fig. 5, specific proton

resonance signals were observed in the range of 5.1 - 5.0 ppm and 1.7 - 1.6 ppm, which were attributed to the L-LA units present in the PLDLs. Additionally, resonance signals at 4.76 ppm, 4.15 ppm, and 2.27 - 0.85 ppm were identified, which originated from the copolymerized PDL units. Furthermore, a peak in the range of 3.59 - 4.0 ppm was observed, corresponding to diethylene glycol, a byproduct resulting from the ring-opening polymerization (ROP) of the monomers.

Based on the ¹H NMR results, the degree of polymerization (DP) of the monomer units, as well as the molar masses of PLDL samples, were calculated in Table 2. The DP was determined by analyzing the ratio of the proton signals of the repeating units in the copolymer chains. The theoretical molar masses of the PLDLs were estimated to be approximately 32-36 kg/mol based on the conversion and weight fraction of L-LA and ε-DL in the copolymers. The ratios were found to be 100:0 in PLLA, 89.5:10.5 in PLDL90, 79.8:20.2 in PLDL80, and 69.5:30.5 in PLDL70. These results align well with the targeted DP values for PLDLs. Thus, it can be concluded that the synthesis of PLDLs was successfully carried out in a direct one-pot process, leading to the desired copolymer compositions. The instantaneous copolymer composition has been traditionally described using the reactivity ratio.

To investigate chemical composition in chains of PLDLs, reactivity ratios

are obtained by comparing the initial comonomer feed and copolymer molecular composition in Table 2. [42] The reactivity ratios of L-LA and DL were calculated using the Mayo-Lewis equation.

$$F_1 = 1 - F_2 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$
(4)

Where r_1 and r_2 are the reactivity ratios of monomers 1 and 2, and f_1 and f_2 are the mole fractions of the feed monomers. These kinetic investigations led to the following values: $r_{LA} = 1.474$ and $r_{DL} = 0.336$. PLLA has a high reactivity ratio (> 1), and PDL has a relatively lower reactivity ratio (< 1). The PLDL series possesses a gradient copolymer structure resulting from composition drift during copolymerization. In the initial polymerization step, the 1-lactide monomers consumed first. As the feed ratio of L-lactide monomer decreases, the ε -decalactone unit s begin to polymerize. The kinetic differences between L-lactide and ε -decalactone induce a blocky copolymer structure. This gradient copolymer imparts unique physical properties to the PLDL series. [43, 44]



Figure 4. FT-IR spectra of synthesized PLLA, PLDL, and PDL.



Figure 5. ¹H NMR spectra of synthesized PLLA and PLDL.

Sample	fpla:pdl	DP_{PLA}	DPpdl	[L-LA]:[ε-DL]	$\mathrm{M}_{\mathrm{n}}^{\mathrm{a}}$	$\mathbf{M}_{n}^{\ b}$	$M_w\!/M_n{}^b$
PLLA	100:0	120.4	0	100:0	34.8k	33.2k	1.95
PLDL90	85:15	103.8	12.2	89.5 : 10.5	34.2k	33.9k	1.96
PLDL80	70:30	85.6	21.7	79.8 : 20.2	32.2k	22.3k	1.65
PLDL70	60:40	72.1	31.7	69.5 : 30.5	31.7k	20.1k	1.64

a : determined by integration ¹H-NMR, b : determined by gel permeation chromatography (GPC) in the sample notation PLDLx, x indicates the molar portion of poly(L-lactide) of copolymers.

Table 2. Characterization data of chemical composition for PLDL series.

3.1.2 Analysis of crystal structure

X-ray diffraction (XRD) patterns were obtained for PLDL samples to analyze their crystalline structure. As shown in Fig. 6, the XRD pattern of the PLLA homopolymer exhibited distinct diffraction at 16.6°, 19.0°, and 22.3°, indicating its semicrystalline nature. These peaks are characteristic of the crystalline regions in PLLA. In contrast, the XRD pattern of PDL showed the absence of any crystalline diffractions, with only a broad peak observed at 2θ of 20.0°. For the PLDL samples, the peak intensity corresponding to the crystalline region of PLLA decreased with an increasing weight percentage of DL incorporated in the copolymer. In PLDL70, only a minimal fraction of the PLLA peaks at 16.6° and 19.0° were observed, indicating a significantly reduced degree of crystallinity. This indicates that the incorporation of alkylbranched moieties of e-DL effectively disrupts the crystalline regions of PLLA by interfering with the chain packing arrangement. Consequently, the preparation of PLDL copolymers by combining PLLA and PDL confirmed the modification of the physical properties of PLLA. The XRD analysis provides evidence of the alteration in the crystalline structure and degree of crystallinity of PLLA upon copolymerization with PDL, demonstrating the impact of incorporating PDL on the physical properties of the resulting PLDL copolymers.



Figure 6. XRD patterns of synthesized PLLA and eDL, and PLDL samples.

3.1.3 Analysis of thermal properties

Thermal stabilities of the PLDL series were evaluated by TGA. Fig. 7 exhibits the thermal degradation behavior under elevated temperature. The PLLA degraded first caused by low thermal stability. On the other hand, the PDL showed the highest degradation temperature, indicating intrinsic thermal stability. The difference in degradation temperature ($T_{d,50\%}$) is approximately 96.0 °C. Therefore, the thermal stabilities of PLDLs were improved as the PDL portion increased. The temperature where 50 wt% of the homopolymer and copolymer series were 234.6 °C for PLLA, 266.9 °C for PLDL90, 295.9 °C for PLDL80, 298.0 °C for PLDL70, and 330.6 °C for PDL. The gradient copolymer composition in PLDLs induced one-step thermal degradation with enhanced thermal stability of PLLA.

DSC was used to investigate the thermal properties of the samples. Fig. 8 shows DSC thermograms of all samples. The parameters obtained from the investigation are summarized in Table. By comparing the melting enthalpies of synthesized PLDLs with 100 % crystalline PLLA, the crystallinity (xc) of each sample was calculated. In the DSC thermograms, decreased crystallinity and melting temperature in PLDLs compared with PLLA were observed due
to the weaker molecular interactions by the butyl chain of PDL. In addition, composition dependence on T_g could be estimated by the Fox equation for all PLDL samples (6).

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{6}$$

where w_1 and w_2 ($w_1+w_2=1$) are the weight fraction of components, T_{g1} and T_{g2} represent the glass transition temperature of each component. There is an excellent agreement between the experimentally determined T_g and those predicted using the Fox equation which are displayed in Table 3. That is, while PLDLs exhibited tapered block composition, they also displayed statistical copolymers. Moreover, having physical properties of gradient copolymer structure, PLDLs have one broad glass transition temperature range. This implied that PLDLs would have an energy-damping property and a broader temperature range. Especially, PLDL80 and PLDL70 exhibited broad T_g around room temperature, with the highest damping performance in room temperature (around 25 °C) as sound absorbers.



Figure 7. Thermal degradation behaviors of PLLA, PDL, and PLDL.



Figure 8. DSC thermograms of synthesized PLLA, PDL, and PLDL.

	calcd Tg[ºc]	Tg(DSC)[⁰C]	T _g width [⁰c]	X _c [%]
PLLA	55.4	55.4	4.9	46.5
PLDL90	39.3	41.8	8.3	33.4
PLDL80	24.2	24.8	10.1	18.9
PLDL70	11.8	12.3	20.1	3.4
PDL	-55.3	-55.3	2.5	-

Table 3. Thermal properties of neat PLLA, PDL, and PLDL.

3.2. Characterization of PLDL foam

3.2.1. Density and porosity

The PLDL foams were produced using thermally-induced phase separation and lyophilization techniques. Where the molar composition of PDL exceeded 0.3, the PLDLs were viscous liquids at room temperature. Therefore, PLLA to PLDL70 were fabricated as hierarchical microcellular foams. The picture of prepared foam samples, measured density, and calculated porosity are shown in Fig. 9. The fabricated foams exhibited a low bulk density of less than 80 kg/m^3 , similar to commercially available sound-absorbing polymer foams. The measured bulk densities of the foams were as follows: 70.33 for PLLA, 72.13 for PLDL90, 77.66 for PLDL80, and 79.04 kg/m³ for PLDL70. Porosity was determined by measuring the mass and volume of the foams and using the density of PLDL copolymers for calculations. All the foams showed high porosity, ranging from 93.0% to 94.2%. The porosity slightly decreased with the increasing proportion of amorphous flexible PDL, as this led to contraction during the lyophilization process. The porosity slightly decreased with the proportion of amorphous flexible PDL present, which induces contraction during the lyophilization process. Despite this contraction, because DL has lower porosity (0.97g/cm³) than PLLA (1.20g/cm³), all samples have high porosity of over 0.9.



Figure 9. (a) PLLA and PLDL foams (b) Apparent density and calculated open porosity.

3.2.2. Pore morphology and size distribution

Representative SEM images of the foams are shown in Fig. 10. The PLLA, PLDL90, PLDL80 and PLDL70 foams formed both microscale major pores and minor pores. This size distribution implies that all foam samples were successfully prepared with hierarchical pore structures. In the SEM image, the major pore cell size exceeding 10 μ m with the surrounding minor pore size below several micrometers was observed.

To analyze the pore size distribution of foams, mercury intrusion porosimetry (MIP), and ¹H NMR cryoporometry analysis are conducted. The mercury intrusion porosimetry data is presented in Fig. 11. The results display a major peak of around 100 μ m and a small shoulder of around 10 μ m. The peak around 100 μ m corresponds to the major pores which occupy most volume fraction, whereas the shoulder peak under 10 μ m corresponds to minor pores embracing larger pores. All the PLDL foams exhibited a similar average pore size on the micrometer scale, with an average of approximately 27.19 \pm 0.6 μ m.

The minor pore which is smaller than 1 um poorly detected in PLDL samples in MIP, due to the pore compression occurring in high intrusion pressure. When the intrusion pressure is higher than critical pressure (P_c), the buckling prevails over mercury intrusion into the pore (D_c). The Pc and Dc is

closely related to the elastic modulus of the sample. With an increasing molar portion of PDL, the amorphous chain of PDL lower the elastic modulus, thus inducing larger critical diameters in MIP analysis. Therefore, pores smaller than 1 um are poorly detected in PLDL samples with low elastic modulus. [45] Therefore, to specify pore size distribution (PSD) and average cell size smaller than 1 µm, non-destructive inspection is required. [46] Solid-state ¹H NMR cryoporometry is an effective method to demonstrate porous polymeric matrices such as polymeric foams, hydrogels, and membranes. [47-49] This approach utilizes melting point depression (ΔT_m) of a probe solvent confined in small pores, which is varied by the size of pores. A small pore has more surface interaction with liquid, inducing a lowered melting temperature. From the Gibbs-Thomson equation, it can be theoretically explained as equation (7).

$$\Delta T_m(D) = T_m - T_m(D) = \frac{4\sigma_{sl}T_m}{D\Delta H_f \rho_s} = \frac{K}{D} \quad (7)$$

where T_m is the melting point of the bulk material, $T_m(D)$ is the melting point of the material with the pore size D, σ_{sl} is the surface energy, ΔH_f is the bulk enthalpy of melting, ρ_s is the solid density. In this study, cyclohexane, of which K is approximately 178 K nm was used as a probe liquid, being suitable for the characterization of hydrophobic PLDL samples. The difference between the normal and the lowered melting point was inversely proportional to a dimension of the minor pores of the foams. By slowly raise temperature after completely freezing the samples, the phase transition of probe solvent causes NMR spin-echo signal measured as a function of temperature. The pore size distribution (dV/dD) can be estimated from the derivative of the intensity-temperature curves as depicted in the following Equation (8).

$$\frac{dI}{dD} = \frac{dV}{dD} = \frac{dV}{dT_m(D)} \frac{dT_m(D)}{dD} \tag{8}$$

V is the signal intensity, which indicates the amount of melted cyclohexane trapped in the pores at the particular temperature, *T*. Fig. 12 displays that the signal intensity smoothly increased in a range of 200-280 *K*. From Eq. (8), $dT_m(D)/dD = K/D^2$ is obtained, thus the above can be rewritten as the following Equation (9).

$$\frac{dV}{dD} = \frac{K}{D^2} \frac{dV}{dT_m(D)} \tag{9}$$

The PSD and the average pore size of minor pores can be estimated from the melting point depression. As shown in Fig. 13, The result curve well matched with the MIP results in PLLA sample. The PLDL foam samples exhibit a similar minor pore size distribution, indicating a consistent pore structure throughout the 30 - 150 nm range. Specifically, PLLA has an

average minor pore size of 65.3 nm, while PLDL90 has 57.8 nm, PLDL80 has 52.8 nm, and PLDL70 has 53.6 nm.

The hierarchical multimodal cell distribution shown from the mercury porosimeter and ¹H NMR cryoporometry is in good agreement with the SEM image. The coexistence of major and minor pores plays a significant role in enhancing the broadband sound absorbing performance, particularly in the low-mid frequency range. The major pore allows more sound waves to enter without surface sound reflection. On the other hand, the minor pore enhances pore complexity, which is closely related to increased surface area by meeting the pore size requirements and having the appropriate distribution of major and minor pores, the samples can effectively absorb sound energy across a broad range of frequencies, making them suitable for broadband acoustic attenuation applications. Therefore, all the samples are meeting the pore size requirement.



Figure 10. SEM images of PLDL foams. x500 and x3000.

Figure 11. Mercury intrusion porosimetry data for PLDL foams.

Figure 12. NMR melting curve for the PLDL foams swollen with

cyclohexane.

Figure 13. NMR pore size distribution obtained using dV/dD of the melting curve data.

3.3. Attenuation properties of PLDL

3.3.1. Damping properties of PLDL with temperature

The damping properties of the PLDL films were investigated using dynamic mechanical analysis (DMA) test. Under applied stress with constant frequency, the polymer behaves as a rigid glass under glass transition temperature. As the temperature gradually rises, inducing segmental motion with higher energy, the mobility of the molecules increases. Then both the loss modulus and the loss factor increase. The energy dissipation mechanism is strongly related to loss modulus (E"), and loss factor (tan δ). The loss modulus is related to the viscous response to external energy, which induces internal friction and thermal dissipation of the material. The tangent delta is a dimensionless quantity that represents the ratio of the loss modulus to the storage modulus of a material. The tan δ can be calculated from the loss modulus. It is a measure of the material's damping capacity or energy dissipation capability. In the context of sound absorption, the tan δ provides information about the material's ability to convert sound energy into heat energy. Higher value and width of tan δ peak in DMA results indicate greater energy dissipation and damping within the material. The loss modulus of the samples displayed as a function of temperature in Fig. 14 a). The loss modulus of PLLA is around 150 MPa and the loss modulus increases as the more PDL

is introduced in copolymer. This is because the alkyl chains in the PDL reduce the tightness of packing, leading to increased molecular mobility at similar molecular weights.

The loss modulus and tan δ of the PLDL film samples were collected with increasing temperature at the constant frequency (1 Hz). Fig. 14 b) shows the tan δ with increasing temperature. Similar to the increase in the loss modulus, tan δ also further increases due to enhanced molecular mobility. The PLLA showed tan δ value at 0.11, PLDL90 for 0.24, PLDL80 for 0.30, and PLDL70 for 0.34. Additionally, tan delta can provide information about the glass transition behavior. The PDL lowers the glass transition temperature due to its low glass transition temperature (-55 °C), resulting in a decrease in the glass transition temperature of the copolymer. As a characteristic of gradient copolymers, they exhibit a broad distribution of glass transition temperatures [50], which leads to a wide T_g width for PLDL copolymers. The PLDL80 and PLDL70 exhibited high tan δ values near room temperature, and they are suitable for use as acoustic absorption materials.

To measure the energy required to induce segmental motion in PLDL samples, the activation energy of the samples is obtained by plotting the varied glass transition temperature by increasing frequency at 1, 2, 5, 10, and 15 Hz. As displayed in Fig. 15, the relationship between logarithmic frequency and the inverse T_g follows a linear trend, indicating that the relaxation processes associated with the glass transition follow an Arrhenius-type behavior. The activation energy of PLLA, PLDL90, PLDL80, and PLDL70 was 327.6, 320.2, 306.7, and 272.6 kJ/mol respectively. Indeed, PDL in the PLDL copolymer leads to a decrease in the energy required to induce molecular motion. This enables the copolymer to more effectively dissipate external acoustic energy. With enhanced molecular mobility and reduced energy barriers for motion, the copolymer becomes more capable of absorbing and attenuating external noise energy. This behavior aligns with the previous findings regarding the increased loss modulus, tan delta, and the broader glass transition temperature distribution, all of which contribute to the copolymer's improved ability to counteract and mitigate external noise.

Figure 14. (a) Temperature-dependent loss modulus (E") and (b) loss factor (tan δ).

Figure 15. Arrhenius plots of the applied frequencies as a function of Tg.

3.3.2. Damping properties of PLDL with frequency

The damping properties as a function of noise frequency (1-20000 Hz) are investigated. A typical temperature for sound absorption foams is around room temperature (25 °C). Therefore, DMA at isothermal condition around 25 °C with frequency sweep mode were tested. The applied frequency range was 1-100 Hz. This way, the damping properties of the samples at a temperature different from their glass transition temperature can be rated. Fig. 16 and Fig. 17 show the loss modulus (E'') and the specific loss factor (tan δ) as a function of frequency. Using the time-temperature superposition (TTS) method, the data extended the frequency-dependent damping properties at room temperature. To analyze the temperature and frequency dependence, we used the shift factor (at) of each sample for superposition from the function of temperature to the function of frequency. When the reference temperature (Tr) is higher than the glass transition temperature of the sample, the shift factor (at) determined using the Williams-Landel-Ferry (WLF) equation. (10) On the other hand, when Tr is lower than the glass transition temperature of the sample, the shift factor can be obtained using the Arrhenius law. (11)

$$\log(a_T) = -\frac{c_1 \times (T - TRef)}{c_2 + (T - TRef)}$$
(10)
$$\log(a_T) = -\frac{E_a}{2.303R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)$$
(11)

These methods allow us to account for the effects of temperature and frequency on the viscoelastic behavior of the material and facilitate the construction of master curves for a broader frequency range.

Fig. 16 a) shows the loss modulus of PLDL70 calculated by the TTS method as a function of the frequency between 1 Hz and 100 Hz at different temperatures. By selecting a reference temperature of 25°C, we constructed the master curve for PLDL70 based on the results shown in Fig. 16 b). The frequency-dependent behavior of the loss factor of PLDL70 at different temperatures is depicted in Fig. 17 a). Utilizing the obtained data, the master curve for PLDL70 was generated, as shown in Fig. 17 b).

Similarly, we applied this methodology to PLLA, PLDL90, and PLDL80, resulting in their respective master curves for the damping factor (tan δ). The master curves displayed in Fig. 18 provide the viscoelastic properties of the foams across a wide frequency range. In the case of PLDL70, the results indicate an increasing damping factor within the frequency range of 0.1 Hz to 20,000 Hz as the proportion of PDL in the copolymer increases. This suggests that the incorporation of PDL enhances the energy dissipation and damping of the foam structures across a broader frequency spectrum.

Figure 16. a) Loss modulus PLDL70 films at different temperatures, b) the TTS master curve of the loss modulus

(at 25°C).

Figure 17. a) Tan δ of PLDL70 at different temperatures, b) the TTS master curve of the tan δ (at 25 °C).

Figure 18. The master curves of the loss factors of PLLA, PLDL90,

PLDL80, and PLDL70 (at 25 °C).

3.3.3 Sound absorption coefficient of PLDL series

The sound absorption coefficient of PLDL foams was measured at various frequencies with a thickness of 20mm, as shown in Fig. 19 a). It was observed that all PLDL foams exhibited improved sound absorption performance compared to commercial PU foams. This improvement can be attributed to the higher energy-damping property of the foam matrix and the presence of a hierarchical pore structure. The hierarchical matrix structure plays a significant role in enhancing sound absorption performance. The friction between air fluids and the pore walls is increased, leading to the conversion of more sound energy into kinetic energy. This is facilitated by the elongated pore pathways created by the smaller minor pores. The viscoelastic behavior of the foam also contributes to its sound absorption properties. The increased loss modulus and damping factor of PLDLs, as observed in dynamic mechanical analysis (DMA) results, are associated with energy dissipation and result in enhanced sound absorption properties. With an increasing proportion of PDL in PLDLs, the energy required to induce segmental motion is lowered. This enables more sound energy to be converted to thermal energy on the surfaces of the polymer foams, leading to improved sound absorption performance across the frequency range.

The noise reduction coefficient (NRC), which assesses sound absorption performance in the low to mid frequencies, aligns with the dynamic mechanical analysis (DMA) results. Fig. 19 b) illustrates that the NRC and average sound absorption values tend to increase as the proportion of PDL in PLDLs increases. The NRC values were 0.20 for PLLA, 0.28 for PLDL90, 0.30 for PLDL80, and 0.33 for PLDL70. Notably, PLDL70 exhibited a substantial 66% improvement in NRC compared to PLLA, highlighting the significant influence of viscoelasticity on sound attenuation in the low to mid frequency range.

Additionally, the average sound absorption coefficient was calculated. The average absorption coefficient for PLLA was 0.35, PLDL90 for 0.42, for PLDL80 for 0.43, PLDL70 for 0.45. The higher value of the average absorption coefficient compared to the NRC for PLDL foams indicates its consideration of sound absorption performance in the high frequency region. Furthermore, the average absorption coefficient increased in PLDL70, contributing to enhanced sound absorption in both lower and higher frequencies.

Furthermore, the quasi-perfect sound absorption range, where the sound absorption coefficient (SAC) exceeds 0.9, was evaluated to assess the broadband sound absorption performance. PLDLs demonstrate a broad perfect sound absorption range (>1000 Hz). The perfect absorption bandwidth of PLLA was 1422 Hz, while the copolymer foams exhibited wider bandwidths of 2133 Hz, 2610 Hz, and 2650 Hz, respectively. Notably, PLDL70 exhibits an almost two-fold wider range of perfect absorption compared to PLLA. These findings indicate that the sound absorption efficiency of the foams depends not only on the pore structure but also on their viscoelastic behavior. Overall, the combination of the hierarchical pore structure and the viscoelastic properties of PLDL foams contributes to their improved sound absorption performance, making them suitable for broadband sound absorption applications.

(b)

sample	NRC	Perfect absorption Range
PLLA	0.20	1422 Hz
PLDL90	0.28	2133 Hz
PLDL80	0.30	2610 Hz
PLDL70	0.32	2650 Hz

Figure 19. (a) sound absorption coefficient in 125-6400Hz, (b) NRC and average sound absorption coefficient

3.3.4. Sound absorption coefficient of PLDL70 foams with different thicknesses

Fig. 20 a) presents the sound absorption coefficient of PLDL70 foams with different thicknesses. Initially, it is observed that the overall sound absorption behavior of the foams improves as the thickness of the samples increases. This trend is consistent with the general behavior observed in porous materials, where increased thickness typically leads to enhanced sound absorption. Furthermore, as the thickness of the foams increases, there is a noticeable shift in the peak absorption frequency towards lower frequencies. This implies that thicker foams tend to exhibit peak absorption at lower frequencies. Consequently, if the sole consideration is broadband sound absorption, thicker foams would demonstrate superior sound absorption performance. However, from a practical standpoint, when using acoustic foams, it is essential to balance sound absorption performance, thickness, and material usage. Achieving higher sound absorption across a broad frequency range while minimizing the thickness and weight of the foams becomes a key objective. This optimization allows for efficient sound absorption while reducing material requirements for practical applications.

In Fig. 20 b), it is observed that commercially available PU foams, when compared to PLDL70 foams with a thickness of 20mm, exhibit lower sound

absorption performance in the broadband range. The PU foam with a thickness of 20mm has an NRC of 0.21, which is comparable to the NRC of the PLDL70 foam with a thickness of 10mm. However, the PLDL70 foam with a thickness of 10mm shows better absorption in the high-frequency range compared to the PU foam. Considering that PU foam has a density of approximately 58 kg/m3, replacing PU foam with PLDL70 foam with a thickness of 10mm would result in a volume reduction of approximately 50% and a weight reduction of 30% while achieving similar sound absorption performance as PU foam with a thickness of 20mm. This demonstrates the practical efficiency of PLDL70 foam as a promising sound-absorbing material for use in automobiles.

Figure 20. (a) sound absorption coefficient of PLDL70 at 500-6400Hz with different thicknesses. (b) sound absorption comparison PLDL70 foam and commercial PU foam.

4. Conclusion

The present research successfully synthesized PLDL through the ring-opening copolymerization of L-lactide and ε -decalactone. The incorporation of PDL in the copolymer played a crucial role in controlling the pore morphology and performance of PLDL foams. The gradient copolymer structure of PLDLs resulted in the formation of microscale hierarchical pores, introducing tortuosity that enhanced sound absorption in the low to mid-frequency range. The flexible alkyl chain of PDL contributed to increased sound energy damping over a broad temperature and frequency range.

Importantly, PLDL foams exhibited significantly improved sound absorption properties compared to bare PLA foam and commercial PU foam, making them suitable for application as automobile sound absorbers. These findings are particularly significant as the PLDL foams are fully based on biopolymers, offering an alternative to petroleum-based polymers traditionally used in sound absorbers. The PLDL sound absorption material, derived from the copolymerization of PLA and PDL with a gradient copolymer structure, holds promise as a sustainable and environmentally friendly alternative to petroleum-based sound absorbers.

5. References

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국문 초록

차량 운행 중에는 차량과 노면의 마찰, 그리고 공기와의 마찰로 인해 넓은 주파수의 소음이 발생하기 때문에 흡음재를 사용한다. 이러한 흡음재 중, 밀도가 낮고 고주파음 흡음 성능이 뛰어난 고분자 폼 소재의 흡음 주파수 영역을 확장하 기 위한 연구가 진행되고 있다. 상용화된 흡음 폼 소재는 PU, melamine 등의 석유 기반 고분자 물질들이 대부분을 차지한다. 그러나 상용 고분자 폼은 에너지 감쇠 거동이 떨어져 중·저주파 음의 흡음 성능이 저하된다는 단점이 있다. 또한 최근 자동차 업계에서 바이오 플라스틱의 도입량이 꾸준히 높아지는 추세에서, 자연 유래고분자의 도입이 시도되고 있다. 자연유래 고분자 중 하나인 PLA은 높은 loss factor를 가져 에너지 감쇠 성능을 높여 중·저주파 음의 흡음 성능을 개선시킬 수 있는 소재이다. 또한 PLA의 기존 단점이었던 취성을 극복하고, 분자의 점탄성 거동을 통한 에너지 소산을 향상하기 위해 자연 유래 고분자인 Poly(ɛ-decalactone) 을 공중합하여 공중합 비율을 조절하였다. 그리고 만들어진 공중합체를 친환경 공법인 열 유도 상분리법을 통해 계층구조형 기공 분포를 가진 폼으로 제작하여 중·저주파 음의 흡음 성능을 더욱 향상하고자 하였다. 이러한 기공 구조와 공중 합체 재료의 향상된 점탄성 에너지 소산 거동을 통해 광대역 주파수에서 흡음 성 능을 개선할 수 있었으며, 20 mm 두께의 폼에서 최대 0.33의 소음저감계수를 달 성하여 친환경적인 흡음 소재를 제작하였다.

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