Efficient, Green, and Low-Cost Conversion of Bivalve-Shell Wastes to Value-Added Calcium Lactate

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ABSTRACT: This work presents the efficient, green, and low-cost preparation of calcium lactate by using bivalve-shell wastes (cockle, mussel, and oyster shells) as raw materials. Three bivalve shells, a cockle, mussel, and oyster, were used separately as an alternative calcium-source material for the preparation of calcium lactate. The bivalve-shell waste was cleaned and milled, obtaining calcium carbonate ($CaCO_3$) powder, which reacted to the lactic acid, forming calcium lactate. The effects of different calcium sources (cockle, mussel, and oyster) and different lactic acid concentrations (6, 8, and 10 mol/L) on the physicochemical properties of the synthesized calcium lactates were then investigated. The results pointed out that the highest solubility of the product was observed when 6 mol/L lactic acid and cockle-shell derived $CaCO_3$ were employed for the calcium lactate preparation. The thermal decompositions of all calcium lactates occurred in three processes: dehydration, ethyl-lactate elimination, and decarbonization, respectively. The results, obtained from an infrared spectrometer, X-ray diffractometer, thermogravimetric analyzer, and scanning electron microscope, confirmed the formation of calcium lactate pentahydrate ($Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$). The diffractograms also indicated the presence of two enantiomers of $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$, namely, of DL- and L-enantiomers, which depended on the lactic acid concentration used in the preparation process. The morphologies of calcium lactates show the firewood-like crystals in different microsizes, together with smaller irregular crystals. In summary, this work reports an effective process to prepare the valuable calcium lactates by using the cheap bivalve-shell-derived $CaCO_3$ as a renewable calcium source.
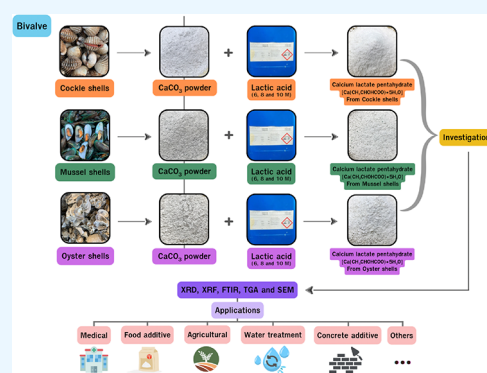
1. INTRODUCTION

The development of green products from biowastes is significantly increasing,[1,2] and the recycling of biowastes is in line with many developing countries with the ambient solving environmental issues.[3] The transformation of biowastes into value-added products is one of the green methods.[4] Aquaculture is an important occupation in Southeast Asian regions, especially Thailand, and the aquaculture animals such as fish, shrimp, and mollusks are essential protein sources.[5] According to the data reported by the United Nations Environment Programme (UNEP), food waste of around 931 million tons is globally produced each year.[6] In 2018, world mollusk production, especially bivalve shells, reached 17.7 million tons.[2] Based on the Food and Agriculture Organization (FAO) of the United Nations (UN) data, more than 70% is represented by clams, oysters, scallops, and mussel shells.[2] Clam (38%) and oyster (33%) shells are the first two wildly globally cultured, followed by scallops (17%) and mussels (13%).[7] In 2021, the quantities of cockle, mussel, and oyster shells from aquaculture farms in Thailand were 33,526, 52,067, and 13,317 t, respectively.[8] A large volume of

post-consumption residues is then generated. More than 10 million tons of bivalve-shell wastes are globally generated each year and generally dumped in landfills,[9] causing environmental issues such as an unwanted smell and contaminated area caused by the decomposition of shells' organics as well as other visual pollutions.[10] These waste sources are a source of greenhouse emissions that affected global warming, which represents a big problem nowadays. Therefore, generating sustainability techniques for mollusk-based waste reduction will contribute to solving environmental issues.[2,11]

Food waste such as bivalve waste is one of the interesting topics for creating a resource-efficient, zero-waste, and carbon-neutral circular economy and developing sustainable investment.[12] Many bivalve-based product manufacturers as well as

many restaurants along Thailand's coast discharge lots of bivalve-based wastes.[13] Consequently, green and effective technologies are required to reduce various environmental problems,[14] caused by bivalve-based wastes. Moreover, marine waste biorefineries will significantly impact all the sustainable development goals (SDGs), which is not a new concept because of the many reports performed about recycling mainly fish and seafood wastes to advanced materials such as chitin, chitosan, and high-purity calcium carbonate.[15−17] Recycling is the most-green and effective method for transforming waste into valuable calcium compounds, especially calcium lactate.[2,18] Calcium lactate is composed of two lactate ($CH_3CHOHCO_2^-$) anions and one calcium (Ca^{2+}) cation. Two crystal forms, namely, calcium lactate pentahydrate ($Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$)[19,20] and calcium lactate monohydrate ($Ca(CH_3CHOHCOO)_2 \cdot H_2O$),[21] were previously reported in the literature. Calcium lactates have been employed as an antidote for soluble fluoride ingestion,[22] for hypocalcemia,[23] for prevention of tetany, as an anti-tartar agent in some mouthwashes and toothpaste, as an antacid,[24] and as a calcium source for treating calcium deficiencies.[18] Calcium lactates have also been employed as food additive material, stabilizer, thickener, nutritional supplement,[25] calcium source for animals and plants,[26] precipitating agent for suspended-solid removal from water,[27] and enhancer to increase the compressive strength and reduce the water permeability of concrete.[28] For the material chemistry, calcium lactate was used as raw material to synthesize advanced compounds such as calcium-containing polymer compounds (urethane, poly-(vinyl alcohol), poly(urethane-urea)s).[29]

Mititelu et al.[18] synthesized calcium lactate by using the Black Sea mussel shell (collected from the Romanian Black Sea coast) as a raw material. The mussel-shell flesh and its shells were first separated, and the obtained shells were rinsed, dried, and then ball-milled. The powder was deproteinized using a 1% KOH solution and then treated with a 30% lactic acid solution. Han et al.[30] prepared calcium lactate with a combination of lactic acid and crab-shell-derived powder. First, the waste powder was deproteinized by basic electrolyzed water (BEW) treatment prepared with 1% NaCl solution. Using this deproteinization, 90.54% of the protein was removed. The researchers also observed that the optimal conditions to prepare calcium lactate compound were a solid-to-liquid (crab-shell-derived powder to lactic acid) ratio of 1:10 g/mL. The researchers observed that 1 g of the shell powder generated 0.89 g of calcium lactate powders, which is the highest production yield (89%). Yu-e[31] hydrothermally synthesized calcium lactate by using eggshell waste as raw material. The researcher also investigated the influences of reaction temperature, reaction time, waste powder-to-lactic acid ratio, excessive rate of eggshell, and eggshell isolation on the calcium lactate production yield. The results showed that the reaction temperature of 100 °C, reaction time of 5 h, waste powder-to-lactic acid ratio of 1:17 g/mL, excessive rate of the eggshell of 60%, stationary time of 15 min in eggshell isolation, and stirring time of 10 min provided the highest calcium lactate production yield (94.66%). Yoon et al.[20] prepared calcium lactate by using a butter-clam shell as a natural calcium resource. The optimal preparation condition was examined by the response surface methodology (RSM). The researchers observed that the solubility and the production yield decreased with increasing molar ratios of calcined butter-clam shell powder. The infrared absorption spectroscopic data indicated

that the reaction product between butter-clam shell powder and lactic acid was $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$, whereas the scanning electron microscopic result showed an irregular microstructural particle. Recently, Seesanong et al.[21] prepared calcium lactate ($Ca(C_2H_4OHCOO)_2$) by using scallop shells with various lactic acid concentrations (40−70%), and the physicochemical properties of scallop-derived calcium lactate were then reported.

However, the differences in the synthesis methods and starting materials are important influencers on the physicochemical characteristics of calcium lactate products.[18,21] Bivalve-shell wastes comprise $CaCO_3$ in the range of 90−96 wt %,[32] promoting them as the green and effective renewable calcium-rich material for sustainable developments, and bio-circular-green economic models are similar research ways in crab shells, lobster, shrimp, and insects.[2,33,34] Therefore, this work aims to synthesize calcium lactate crystals through an efficient, green, and low-cost process by using three different bivalve-shell wastes (cockle, mussel, and oyster), mostly cultured in Thailand, as a renewable material. The solubility and manufacturing characteristics of the synthesized calcium lactates were also investigated to demonstrate the potential of the studied bivalve-shell waste for application as a green and high-value-added renewable calcium-rich material. Each bivalve-shell waste was first cleaned and milled to achieve the shell-derived $CaCO_3$ powder. After that, lactic acid was mixed and reacted to the obtained $CaCO_3$ powder, generating a calcium lactate salt solution, which was then dried, forming calcium lactate powder. All synthesized calcium lactate products were analyzed by an X-ray fluorescent spectrometer, X-ray diffractometer, infrared absorption spectrometer, thermogravimetric analyzer, and scanning electron microscope. The effect of the lactic acid concentration (employed in the salt solution preparation step) on the reaction time, percentage yield, solubility, and crystallography of calcium lactate product was also investigated. The estimation of the emission of CO_2 gas of the calcium lactate obtained from bivalve-shell wastes is reported for the first time.

2. MATERIALS AND METHODS

2.1. Raw Material Preparation. Each bivalve-shell waste was randomly obtained from the food-waste section of the seafood restaurants in Pattaya City, Chonburi province, Thailand. The emission CO_2 of transportation for the bivalve-shell waste was calculated to be equal to 75 km × 1 t × 0.0536 $kgCO_2e$/t km/1000 = 0.004 $kgCO_2e$.[35] A large residual tissue of shells was manually removed. Sodium hypochlorite (NaOCl) solution (reagent grade, 15% Cl_2), obtained from Sigma-Aldrich (EF (emission factor) = 0.7812 $kgCO_2e$/L),[36] was diluted by DI water (EF_{DI} = 2.043 $kgCO_2e$/m³)[34] to obtain 2.5% NaOCl solution. The CO_2 emission of the diluted solution was evaluated at 0.1345 $kgCO_2e$/L. For the deproteinization process, the waste was soaked in a diluted NaOCl solution (mass ratio of shell waste to solution equal 1 to 1.) The waste was then soaked in distilled water three times to complete the cleaning process (about 1 L of DI water for usage). The cleaned waste was dried at a temperature of 105 °C for 3 h, crushed, and milled, achieving bivalve-shell-derived $CaCO_3$ powders (electricity usage, the CO_2 emission = 1.5 kw h × 0.6093 $kgCO_2$ e/kw × 1 kg/100 kg h = 0.0091 $kgCO_2$ e). To homogenize the particle size, $CaCO_3$ powders were sieved using mesh #80 (sieve size: 180 μm) and then sieved again using mesh #120 (sieve size: 120 μm). This sieving process
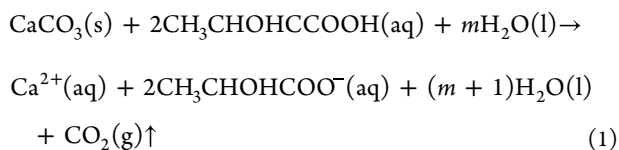
Table 1. Calculation of Carbon Emissions in the Production of Calcium Lactate from the Reaction of the Bio-Green CaCO$_3$ Powder Obtained from Bivalve Shell Wastes and Various Lactic Acid Concentrations[a]

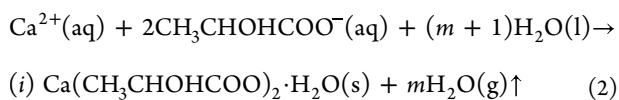| chemical agent	details	quantity	unit	EF	carbon emissions (kgCO$_2$e/kg)
CaCO$_3$(s)	Bio-green CaCO$_3$ from cockle shells (98.10% purity)	1.019	kg	0.1476 kgCO$_2$e/kg	0.1504
	Bio-green CaCO$_3$ from mussel shells (96.30% purity)	1.038	kg	0.1476 kgCO$_2$e/kg	0.1532
	Bio-green CaCO$_3$ from oyster shells (96.60% purity)	1.035	kg	0.1476 kgCO$_2$e/kg	0.1528
	minerals (lime or rock stone) assumed 100% purity	1.000	kg	1.067 kgCO$_2$e/kg	1.0670
CH$_3$CHOHCOOH	13.4 mol·L^{-1}	1.000	L	2.5389 kgCO$_2$e/L	4.3406
	10 mol·L^{-1}	2.00	L	2.1703 kgCO$_2$e/L	4.3402
	8 mol·L^{-1}	2.50	L	1.7361 kgCO$_2$e/L	4.3402
	6 mol·L^{-1}	3.33	L	1.3020 kgCO$_2$e/L	4.3402
Ca(CH$_3$CHOHCOO)$_2$·5H$_2$O (Mw =308 g/mol) obtained from Bio-green CaCO$_3$ from cockle shells (98.10% purity)	CA10 (87.83% yield)	2.71	kg		(0.1504 + 4.3406 + 0.440)/2.71 = 1.8229
	CA8 (83.55% yield)	2.57	kg		(0.1504 + 4.3402 + 0.440)/2.57 = 1.9163
	CA6 (80.59% yield)	2.48	kg		(0.1504 + 4.3402 + 0.440)/2.48 = 1.9867
Ca(CH$_3$CHOHCOO)$_2$·5H$_2$O (Mw =308 g/mol) Bio-green CaCO$_3$ from mussel shells (96.30% purity)	CA10 (85.28% yield)	2.63	kg		(0.1532 + 4.3406 + 0.440)/2.63 = 1.8780
	CA8 (84.77% yield)	2.61	kg		(0.1532 + 4.3402 + 0.440)/2.61 = 1.8894
	CA6 (78.12% yield)	2.41	kg		(0.1532 + 4.3402 + 0.440)/2.41 = 2.0505
Ca(CH$_3$CHOHCOO)$_2$·5H$_2$O (Mw = 308 g/mol) Bio-green CaCO$_3$ from oyster shells (96.60% purity)	CA10 (88.19% yield)	2.72	kg		(0.1528 + 4.3406 + 0.440)/2.72 = 1.8164
	CA8 (88.16% yield)	2.72	kg		(0.1528 + 4.3402 + 0.440)/2.72 = 81,694
	CA6 (80.61% yield)	2.48	kg		(0.1528 + 4.3402 + 0.440)/2.483 = 1.8507
Ca(CH$_3$CHOHCOO)$_2$·5H$_2$O obtained from minerals react with lactic acids assumed 100% yield	10 mol·L^{-1} (100% yield)	3.08	kg		(1.067 + 4.3406 + 0.440)/3.08 = 1.8967
	8 mol·L^{-1} (100% yield)	3.08	kg		(1.067 + 4.3402 + 0.440)/3.08 = 1.8984
	6 mol·L^{-1} (100% yield)	3.08	kg		(1.067 + 4.3402 + 0.440)/3.08 = 1.8984

[a]Remarks: The carbon emissions of various lactic acid concentrations estimated from the dilution of 13.4 mol·L^{-} lactic acid by DI water (EF$_{DI}$ = 0.0020 kgCO$_2$e/L).

resulted in the milled $CaCO_3$ powders with particle sizes from 120 to 180 μm. The CO_2 emission of the production process of the bivalve-shell-derived $CaCO_3$ powders (transportation, chemical and DI water usage, and electricity) is estimated to be about 0.1476 kgCO$_2$e/kg for each shell (cockle, mussel, and oyster shells), which is nearly the emission factor of $CaCO_3$ (food grade at plant, EF = 0.30 kgCO$_2$e/kg). Obtained bivalve-shell-derived $CaCO_3$ powders were then used as raw material for the preparation of calcium lactate. Lactic acid ($CH_3CHOHCOOH$, 88%, d = 1.209 kg/L, ACS grade), obtained from Sigma-Aldrich, was also used as a reagent to prepare the calcium lactate, which currently has the CO_2 emission of 2.1 kg CO_2e/kg or 2.5389 kg CO_2e/L.[37] This ACS reagent was used without an additional purification process. However, before the preparation of calcium lactate, this pristine lactic acid (88% or 11.72 mol/L) was first diluted using distilled water as the solvent, achieving three different concentrations of lactic acids (6, 8, and 10 mol/L). The CO_2 emissions of lactic acids (6, 8, and 10 mol/L) were evaluated at 1.3020, 1.7361, and 2.1703 kg CO_2e/L (Table 1 and Supporting Information). The dilution is an exothermic process; therefore, the diluted acidic solutions were exposed to atmospheric conditions, obtaining room-temperature acidic solution before further use.
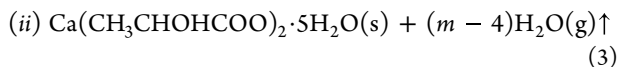
2.2. Calcium Lactate Preparation. Calcium lactate solution containing Ca^{2+} and $CH_3CHOHCOO^-$ ions could be generated from the reaction between $CaCO_3$ and $CH_3CHOHCOOH$ as shown in eq 1:

$$CaCO_3(s) + 2CH_3CHOHCCOOH(aq) + mH_2O(l) \rightarrow$$

$$Ca^{2+}(aq) + 2CH_3CHOHCOO^-(aq) + (m + 1)H_2O(l)$$

$$+ CO_2(g)\uparrow \tag{1}$$

According to a previous work, hydrate forms of calcium lactate crystals, e.g., monohydrate ($Ca(CH_3CHOHCOO)_2 \cdot H_2O$)[18] and pentahydrate $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$[19,20] phases, could be formed from the evaporation process of the aqueous solution, as demonstrated in eqs 2 and 3, respectively.

$$Ca^{2+}(aq) + 2CH_3CHOHCOO^-(aq) + (m + 1)H_2O(l) \rightarrow$$

$$(i)\ Ca(CH_3CHOHCOO)_2 \cdot H_2O(s) + mH_2O(g)\uparrow \tag{2}$$

or

$$(ii)\ Ca(CH_3CHOHCOO)_2 \cdot 5H_2O(s) + (m - 4)H_2O(g)\uparrow \tag{3}$$

Therefore, after the solvent evaporation, the hydrate form of bivalve-shell-derived calcium lactate powder synthesized in this research was investigated and reported. The crystallization process of calcium lactate hydrate was explained. Bivalve-shell-derived powders were weighted, obtaining 100 g of $CaCO_3$ powders. Each acidic concentration solution (6, 8, or 10 mol/L) was slowly poured into a beaker containing $CaCO_3$ powders using the solid-to-liquid mole ratio of 1:2. The mixture was constantly stirred with a magnetic stirrer (C-MAG HS 7, IKA) at 250 rpm until CO_2 gas was not evolved, forming salt solution containing Ca^{2+} and $2CH_3CHOHCOO^-$ ions and releasing thermal energy (an exothermic process). The obtained salt solution was then exposed to an ambient environment to dry itself. Using this drying process, Ca^{2+} and $CH_3CHOHCOO^-$ attracted and formed Ca-($CH_3CHOHCOO)_2$. Furthermore, H_2O in the reaction

process was inserted into the crystal structure of Ca-($CH_3CHOHCOO)_2$, forming $Ca(CH_3CHOHCOO)_2 \cdot nH_2O$ (n = 1 or 5) as shown in eqs 2 or 3. The Ca-($CH_3CHOHCOO)_2 \cdot nH_2O$ samples derived from cockle-shell waste and 6, 8, or 10 mol/L acidic solution were labeled as CL6$_{CS}$, CL8$_{CS}$, or CL10$_{CS}$, respectively. For mussel- or oyster-shell-derived $CaCO_3$ powders, the shell powders were prepared similar to the preparation process of cockle-shell-derived $CaCO_3$. The $Ca(CH_3CHOHCOO)_2 \cdot nH_2O$ samples prepared from the reaction between mussel- or oyster-shell-derived $CaCO_3$ and 6, 8, or 10 mol/L acidic solution were labeled as CL6$_{MS}$, CL8$_{MS}$, and CL10$_{MS}$ or CL6$_{OS}$, CL8$_{OS}$, and CL10$_{OS}$, respectively.

2.3. Characterization. Elemental compositions of all prepared calcium lactate samples were identified and determined by a Bruker SRS 3400 X-ray fluorescence (XRF) spectrometer. The sample crystallography was characterized by a Bruker AXS D8 Advance X-ray diffractometer (XRD). The diffraction database provided by the International Centre for Diffraction Data (ICDD)[38,39] was used to compare and confirm the experimental diffraction patterns of samples prepared in this work. 2θ angles were measured from 5 to 60° with an increment of 0.01° under the scan speed of 1 s/step. A PerkinElmer Spectrum GX Fourier transform infrared (FTIR) spectrophotometer was used to identify the functional groups such as $CH_3CHOHCOO^-$, H_2O, and $Ca-O_8$ octahedral of samples. Infrared absorption spectra were recorded from 4000 to 400 cm^{-1} with the scan number of 32 scans at a resolution of 1 cm^{-1}. Each sample (0.1 mg) was homogeneously mixed with spectroscopic-grade potassium bromide powder (1 mg). The mixture was then pressed, forming a small pellet for FTIR measurement.[34] A PerkinElmer Pyris Diamond TG/DTA analyzer was used for the thermal decomposition investigation of samples. Thermogravimetric (TG) and its differential thermogravimetric (DTG) curves of samples were then recorded from room temperature to 900 °C using a constant heating rate of 10 °C/min. The thermal measurement was conducted under a 99.9% N_2 atmosphere using calcined α-Al_2O_3 as the reference material.[40] Each sample was loaded into an alumina pan without a lid and sample pressing step. A Zeiss LEO VP1450 scanning electron microscope (SEM) was used to image the surface morphology of samples. Before the morphological investigation, samples were sputter coated by gold nanoparticles to prevent the accumulation phenomenon of electric charge in nonconductive solid samples.[41,42]

3. RESULTS AND DISCUSSION

3.1. Production Yield. According to eqs 1−3, the production yield of calcium lactate powders could be calculated by using eq 4:

$$yield\ (\%) = \frac{m_{pro}}{m_{sta}} \times 100 \tag{4}$$

where m_{pro} and m_{sta} are the masses (g) of the reacted product (calcium lactate crystal) and of the starting material ($CaCO_3$ powder), respectively.

Table 2 illustrates the reaction time, production yield, and solubility of calcium lactate products prepared from different bivalve-shell wastes (cockle, mussel, and oyster) and different lactic acid concentrations (6, 8, and 10 mol/L). The term "reaction time" in this context means the time to dissolve

Table 2. Reaction Time, Production Yield, and Solubility of Calcium Lactates (CL) Prepared from Cockle (CS), Mussel (MS), and Oyster (OS) Shells Using 6, 8, and 10 mol/L Lactic Acid

sample	reaction time (s)	production yield (%)	soluble fraction (%)
Cockle-shell derived CLs			
CL6$_{CS}$	125 ± 4	87.83 ± 1.86	97.75 ± 1.46
CL8$_{CS}$	107 ± 5	83.55 ± 1.45	94.16 ± 1.82
CL10$_{CS}$	82 ± 2	80.59 ± 1.54	90.14 ± 1.51
Mussel-shell derived CLs			
CL6$_{MS}$	152 ± 7	85.28 ± 1.35	95.49 ± 1.34
CL8$_{MS}$	125 ± 5	84.77 ± 1.65	93.83 ± 1.47
CL10$_{MS}$	99 ± 3	78.12 ± 1.49	89.71 ± 1.61
Oyster-shell derived CLs			
CL6$_{OS}$	195 ± 9	88.19 ± 1.78	95.61 ± 1.41
CL8$_{OS}$	153 ± 5	88.16 ± 1.64	93.41 ± 1.72
CL10$_{OS}$	110 ± 4	80.61 ± 2.10	91.34 ± 1.36

bivalve-shell-derived $CaCO_3$ powders in the lactic acid solution, forming a calcium lactate solution. Solubility is defined as the amount of synthesized calcium lactate powder (solute) that passes into water (solvent) to achieve an aqueous solution.[43] A shorter reaction time was obtained when the higher lactic acid concentration was used for the production process of calcium lactate solution. As described in Section 2.2 "Calcium Lactate Preparation", a molar ratio between $CaCO_3$ and $CH_3CHOHCOOH$ was set at 1:2 to complete the chemical reaction, which formed Ca^{2+}-2$CH_3CHOHCOO^-$-H_2O systematic solution. In addition, higher lactic acid concentrations mean a higher amount of lactic acid content; therefore, the chemical reacting progress as demonstrated in eq 1 shifted to the right side. For this situation, preparation of Ca^{2+}-2$CH_3CHOHCOO^-$-H_2O solution by using the higher concentrations of lactic acid leads to complete dissolution within a short time. These phenomena were observed in all cases of bivalve-shell-derived $CaCO_3$ powders. Moreover, the dissolution temperatures increased with increasing lactic acid concentrations, pointing out that the dissolution reaction is an exothermic process.

The production yields of the crystalline calcium lactate product derived from cockle, mussel, and oyster shells are in the ranges of 80.59−87.83, 78.12−85.28, and 80.61−88.19%, respectively. These results pointed out that to achieve the highest production yield of calcium lactate crystals on the manufacturing scale, cockle or oyster shells should be selected as a raw renewable material for the calcium lactate preparation process. Furthermore, the production yield decreased with increasing lactic acid concentration and the highest production yield was observed when 6 mol/L lactic acids was added to $CaCO_3$ powder, forming CL6$_{CS,MS,andOS}$ products. The solubility of each calcium lactate powder was additionally investigated. As demonstrated in Table 1, the highest solubility was observed for calcium lactate powder prepared from the reaction between cockle-derived $CaCO_3$ powders and 6 mol/L lactic acid solution. This high solubility property of CL6$_{CS}$ is suitable for the preparation of immediate-release tablets for use as a calcium source for treating calcium deficiencies.[18] The solubility values obtained in this research with the highest value of 97.75% for CL6$_{CS}$ products are in good agreement with the data reported by Yoon et al.[20] They used the butter-clam shell as a calcium source to prepare calcium lactate powders in the pentahydrate from $(Ca(CH_3CHOHCOO)_2$·

5H_2O). They prepared 11 calcium lactate samples, investigated the solubility of each sample, and observed the variable solubility in the range of 93.6−98.5% with an average value of 97.3%.[20] Additionally, the CO_2 emissions for the chemical process of calcium lactates from the bivalve shells were estimated by only chemical usages and found to be 1.82−1.98, 1.88−2.05, and 1.82−1.85 kg CO_2e/kg for the products obtained from the reaction between the bivalve shells (cockle, mussel, and oyster shells) and 8, 10, and 12 mol/L, respectively[35,36] (Table 1). These obtained values of CO_2 emissions for the produced calcium lactate in this work are close to that produced by minerals (lime or rock stones) as raw materials (1.85−1.89 kg CO_2e/kg), but purity and % yield were assumed at 100% to estimate ideally (Table 1 and Supporting Information). If purity and % yield are considered to be below 100% according to reality, the recycling of these bivalve shells to calcium lactate can reduce the CO_2 emissions and limestone/rock ore uses, which are limited resources.

3.2. Elemental Composition. The XRF spectrometer was employed to determine the elemental composition of all prepared samples, and the resulting major and minor elemental compositions of samples derived from cockle, mussel, and oyster shells are demonstrated in Figure 1. In addition, all detected elemental compositions of each calcium lactate sample are listed in Table 3.
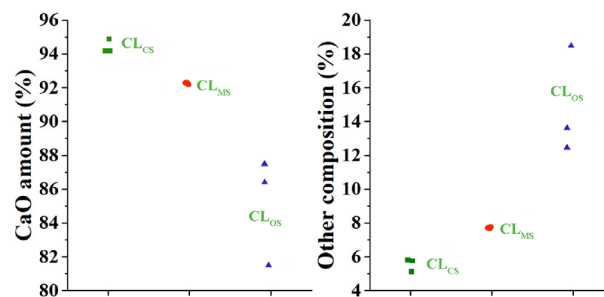

Figure 1. Major (calcium oxide, CaO) and minor (other) elemental compositions of calcium lactates (CL) derived from cockle (CS), mussel (MS), and oyster (OS) shells using 6, 8, and 10 mol/L lactic acid.

As demonstrated in Figure 1, calcium oxide (CaO) is the major component of all calcium lactate products. However, all cockle-shell-derived calcium lactates (CL$_{CS}$) prepared from all lactic acid concentrations (6, 8, and 10 mol/L) showed the highest content of CaO in the range of 94.2−94.9% (Table 3). In contrast, all oyster-shell-derived calcium lactates (CL$_{OS}$) showed the highest content of other elements in the range of 12.46−18.48%. The highest CaO content coupled with the lowest other elements points out the highest purity of calcium lactate product;[21] therefore, it should be mentioned that the production of calcium lactate by using cockle shell as a renewable source provided the highest-purity product when comparing both mussels and oyster shells. As listed in Table 3, oxides of many elements were observed in calcium lactate products (CL$_{MS}$ and CL$_{OS}$) derived from mussel and oyster shells. In contrast, oxides of zinc (Zn), copper (Cu), and nickel (Ni), as well as elemental bromine (Br), were not observed in calcium lactate products (CL$_{CS}$) derived from cockle shells. This result also pointed out the highest-purity phase of cockle-shell-derived calcium lactates. The accumulation of toxic metals such as chromium (Cr), strontium (Sr), cadmium

Table 3. Elements and Their Contents of Calcium Lactates (CL) Prepared from Cockle (CS), Mussel (MS), and Oyster (OS) Shells Using 6, 8, and 10 mol/L Lactic Acid

elements		contents (%)								
		$CL6_{CS}$	$CL8_{CS}$	$CL10_{CS}$	$CL6_{MS}$	$CL8_{MS}$	$CL10_{MS}$	$CL6_{OS}$	$CL8_{OS}$	$CL10_{OS}$
					Major element					
calcium oxide	CaO	94.859	94.227	94.171	92.317	92.287	92.217	87.537	81.524	86.379
					Minor elements					
sodium oxide	Na_2O	0.758	0.792	0.745	1.14	1.04	0.919	0.776	0.887	0.677
magnesium oxide	MgO	0.188	0.193	0.180	0.277	0.298	0.269	2.240	2.990	1.170
alumina	Al_2O_3	0.559	0.682	0.652	0.809	0.856	0.772	0.995	1.720	1.320
silicon dioxide	SiO_2	1.540	1.810	1.770	2.230	2.450	2.160	4.670	8.520	6.320
phosphorus pentoxide	P_2O_5	0.048	0.045	0.057	0.170	0.173	0.173	0.132	0.165	0.145
sulfur trioxide	SO_3	0.163	0.168	0.141	0.643	0.527	0.558	0.936	1.34	1.15
chlorine	Cl	0.016	0.017	0.016	0.065	0.056	0.058	0.765	0.780	0.510
potassium oxide	K_2O	0.023	0.028	0.032	0.030	0.033	0.041	0.155	0.202	0.211
titanium dioxide	TiO_2	0.202	0.189	0.202	0.198	0.231	0.217	0.117	0.126	0.127
manganese oxide	MnO	0.087	0.081	0.094	0.042	0.038	0.049	0.120	0.117	0.107
ferrous oxide	Fe_2O_3	1.140	1.300	1.450	1.190	1.150	1.630	1.040	1.140	1.330
strontium oxide	SrO	0.417	0.468	0.490	0.853	0.820	0.891	0.502	0.454	0.506
bromine	Br				0.036	0.041	0.046	0.015	0.017	0.020
zinc oxide	ZnO								0.018	0.014
copper oxide	CuO									0.014
nickel oxide	NiO					0.014				
total element summation		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
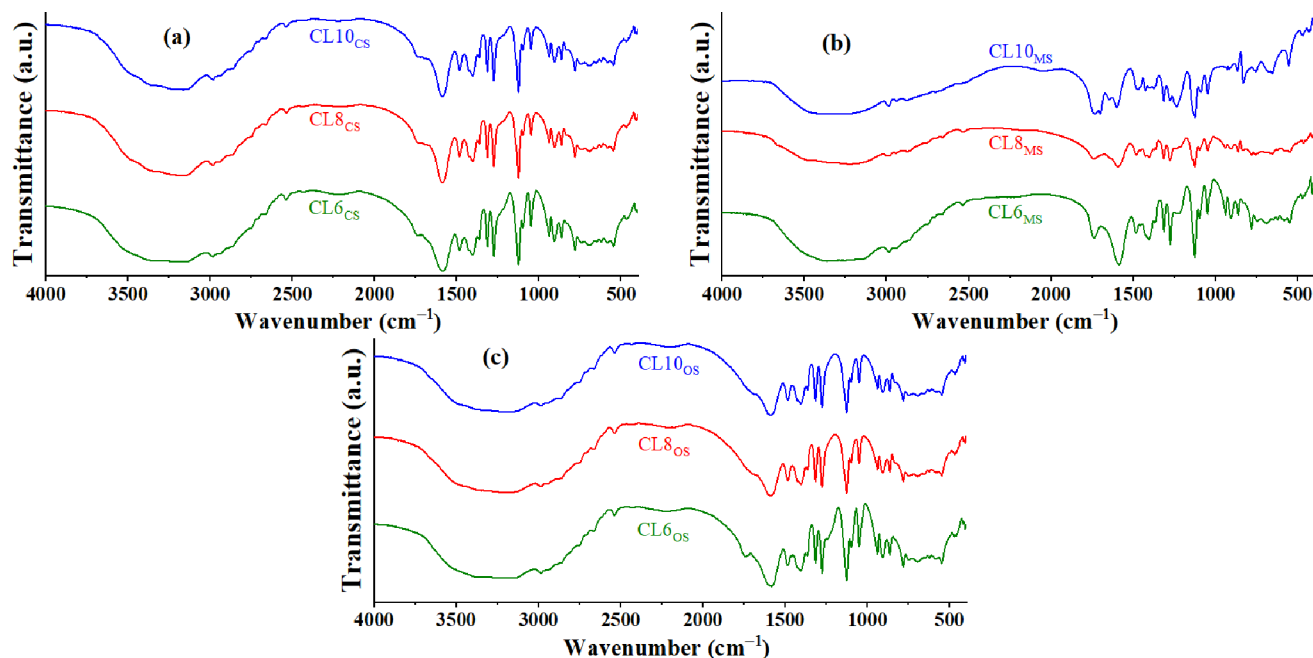
Figure 2. Infrared absorption spectra of calcium lactates (CL) prepared from cockle (CS, a), mussel (MS, b), and oyster (OS, c) shells using 6, 8, and 10 mol/L lactic acid.

(Cd), arsenic (As), and lead (Pb) elements could be found in bivalve shells, which depended on the shells' source.[21,44,45] However, as shown in the XRF results (Table 3), toxic metals were not observed in all calcium lactate products derived from studied bivalve-shell wastes collected from Pattaya's seacoast.

3.3. Vibrational Characteristics. An infrared absorption spectrometer was used to investigate the vibrational characteristics of bivalve-shell-derived calcium lactate products. Figure 2a presents the infrared absorption spectra of cockle-shell-derived calcium lactate products (CL_{CS6}, CL_{CS8}, and CL_{CS10}) prepared at different lactic acid concentrations (6, 8, and 10

mol/L). The absorption spectra of calcium lactates prepared from mussels (CL_{MS6}, CL_{MS8}, and CL_{MS10}) and oysters (CL_{OS6}, CL_{OS8}, and CL_{OS10}) are demonstrated in Figure 2b and c, respectively. All calcium lactates demonstrated similar infrared absorption characteristics, indicating that each synthesized calcium lactate contained the same functional groups such as lactate ($CH_3CHOHCOO^-$), water (H_2O), and the octahedral metal oxide (CaO_8) groups. The vibrational absorption modes of samples were then assigned based on the vibrational characteristics of $CH_3CHOHCOO^-$, H_2O, and Ca−O groups.

The infrared absorption band of 3688−3016 cm^{-1} was assigned as the asymmetric and symmetric stretching modes of O−H of H_2O in the crystal structure of Ca-$(CH_3CHOHCOO)_2 \cdot nH_2O$. The absorption band of 1845−1456 cm^{-1} was assigned as the stretching mode of C=O of the carboxylate $(RCOO^-)$ group of $CH_3CHOHCOO^-$. These positional absorption bands are in agreement with the results reported in the previous works. Pavia et al.[44] summarized and reported various vibrational modes of different functional groups such as $R_2C=O$ (carbonyl group, R = alkyl group). They reported that the infrared absorption band of C=O could be observed in the range of 1850−1650 cm^{-1}. Moreover, Lee and Kim[46] used a black snail (*Semisulcospira bensoni*) as the calcium source to synthesize calcium lactate powders. They then used an infrared absorption spectrometer to characterize and confirm the obtained black-snail-derived calcium lactate product. They assigned the absorption peaks at 1592 and 1430 cm^{-1} as the asymmetric and symmetric stretching modes of the $RCOO^-$ group, respectively. They also assigned the absorption bands of 3030−2852 and 1515−1340 cm^{-1} as the stretching and bending modes of C−H of $CH_3CHOHCOO^-$, respectively.[46] Cheong[47] prepared calcium lactate by using a precipitated $CaCO_3$ in the aragonite single phase as a calcium source. The vibrational properties of calcium lactate were then investigated. The vibrational band of 3500−3000 cm^{-1} was assigned as the asymmetric and symmetric O−H stretching modes of H_2O. The band of 1750−1500 cm^{-1} was assigned as the stretching characteristics of C=O of $CH_3CHOHCOO^-$, whereas the band of 1400−1300 cm^{-1} was assigned as the C−H bending mode of $CH_3CHOHCOO^-$.[47] All vibrational characteristics and their absorption positions of the synthesized calcium lactates are additionally listed in Table 4, confirming that all studied bivalve-shell wastes were successfully used as the renewable natural source to prepare the calcium lactate hydrate with the formula of $Ca(CH_3CHOHCOO)_2 \cdot nH_2O$. The value of n (mole number of H_2O that existed in the crystal

Table 4. Vibrational Characteristics and their Absorption Positions of All the Synthesized Calcium Lactates

vibrational characteristics	positions (cm^{-1})
$CH_3CHOHCOO^-$	
asymmetric C−H stretching of CH_3	3016−2958
symmetric C−H stretching of CH_3	2958−2899
C−H stretching of CH	2899−2829
asymmetric CH_3 bending (twisting)	1511−1451
symmetric CH_3 bending (twisting and rocking)	1376−926
symmetric C−H bending of CH	1336−1244
C−C stretching of C−CH_3	1067−1017
C−C stretching of C−COO^-	884−847
out-of-plane COO^- bending (twisting)	847−768
symmetric C−C bending of C−COH	768−605
out-of-plane COO^- bending (wagging)	605−484
in-plane COO^- bending (rocking)	424−400
H_2O	
asymmetric O−H stretching	3688−3312
symmetric O−H stretching	3312−3016
$CH_3CHOHCOO^-$ and H_2O	
asymmetric and symmetric C=O stretching of COO^-, H−O−H bending of H_2O	1845−1456
CaO_8 octahedral	
Ca−O stretching	484−424

structure of $Ca(CH_3CHOHCOO)_2$) was calculated, and the result is demonstrated and discussed in Section 3.4 "Thermal Decomposition".
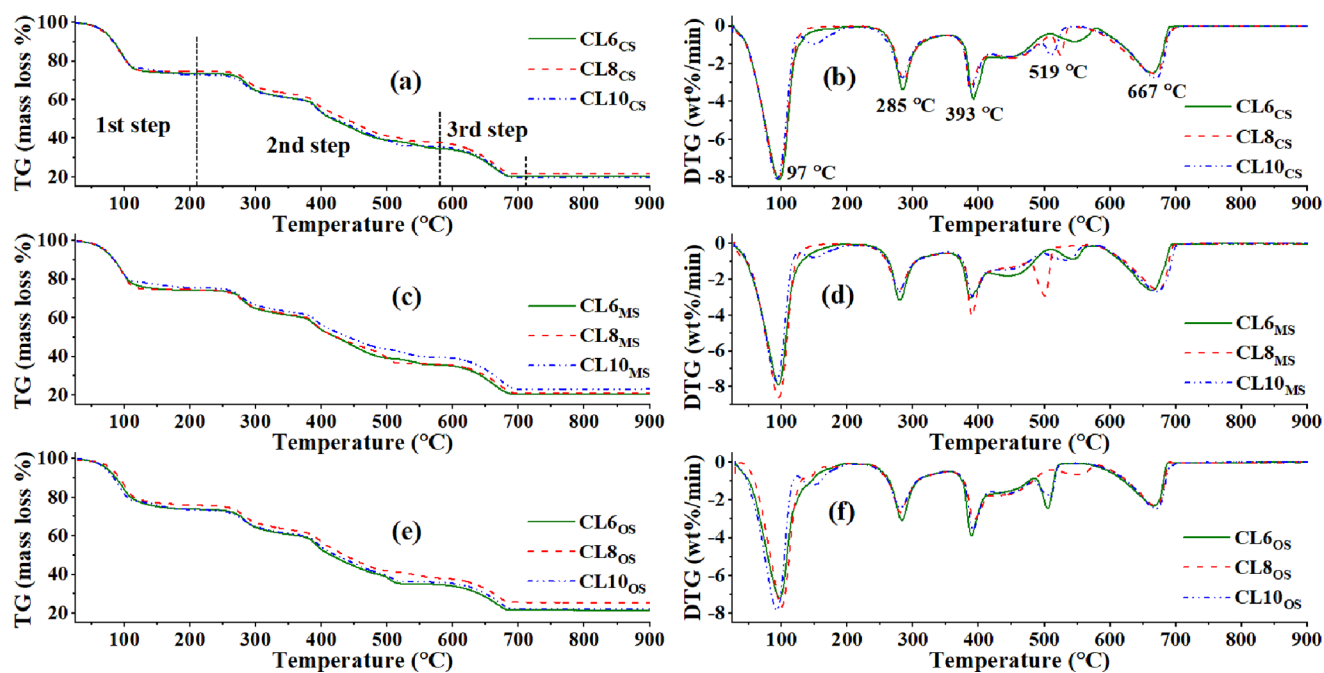
3.4. Thermal Decomposition. The thermal decomposition behaviors of all the synthesized compounds were investigated by the TG analyzer, and the resulting thermal curves were then interpreted. Figure 3 shows the thermal decomposition (TG and DTG) curves in the temperature range of 30−900 °C of calcium lactate samples prepared from cockle (Figure 3a,b), mussel (Figure 3c,d), and oyster (Figure 3e,f) shells, respectively. The thermal characteristics of calcium lactate samples in each CL_{CS}, CL_{MS}, or CL_{OS} group are similar to each other within the group, pointing out that the studied lactic acid concentration ranges (6, 8, and 10 mol/L) and the renewable calcium sources (cockle, mussel, and oyster shells) were successfully used for the preparation of calcium lactates.

As displayed in Figure 3, the thermal decomposition processes (TG-DTG curves) of all calcium lactate compounds presented three decomposition steps in the ranges of 30−210, 210−580, and 580−710 °C, which corresponded to (i) the elimination of H_2O of $Ca(CH_3CHOHCOO)_2 \cdot nH_2O$ to form anhydrous $Ca(CH_3CHOHCOO)_2$,[47,48] (ii) the elimination of $CH_3CHOHCOOC_2H_5$ (ethyl lactate) of Ca-$(CH_3CHOHCOO)_2$ to form $CaCO_3$, and (iii) the elimination of CO_2 of $CaCO_3$ to form CaO,[18] respectively. Considering the $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ formula, its theoretical total mass-loss and residual-mass percentages are equal to 81.81 and 18.19%, respectively. These theoretical values indicated and confirmed that the chemical formula of calcium lactate powders synthesized in this research was Ca-$(CH_3CHOHCOO)_2 \cdot 5H_2O$ (calcium lactate pentahydrate).[19] The slight differences between the experimental and theoretical values of mass-loss and residual-mass percentages may be the influence of moisture that was absorbed on the surface of the samples. Each experimental percentage of the mass loss and residual mass of calcium lactates prepared from cockle, mussel, and oyster shells using three different lactic acid concentrations are listed in Table S3 (Supporting Information). The thermally decomposed mechanisms of calcium lactate in this work are slightly different from calcium lactate obtained from scallop shells in our previous work,[18] and its final decomposed products (CaO) were obtained at lower temperatures (700 < 800 °C).
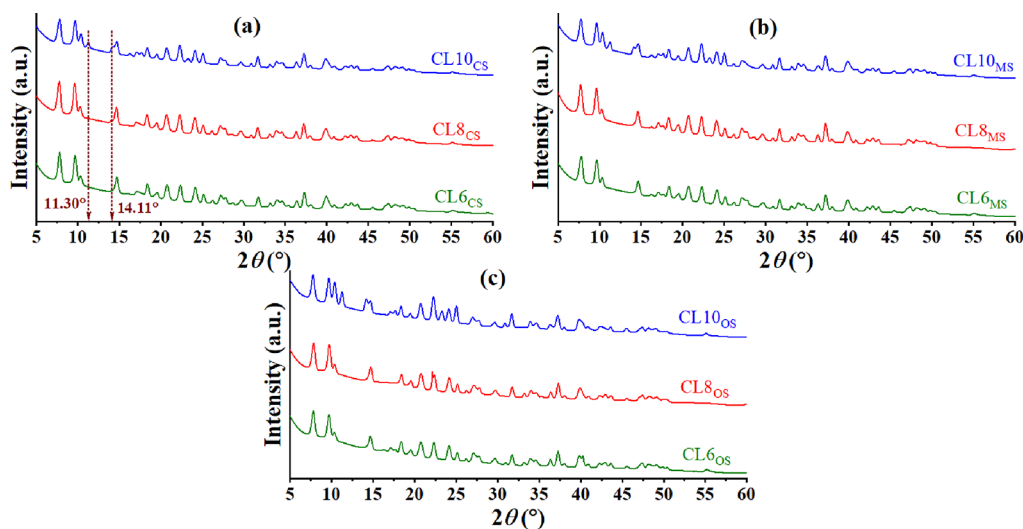
The first thermal decomposition step appeared in the temperature range of 30−210 °C with a TG mass loss of around 26% (theory: 29.22%) and a DTG peak of around 97 °C, which is assigned as the losses of both the adsorbed water that existed on the surface of $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ and the water $(5H_2O)$ that existed in the crystal structure of $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$. The loss of $5H_2O$ from the crystalline $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ structure was also called the "dehydration process". These two losing processes of water resulted in the formation of $Ca(CH_3CHOHCOO)_2$.[47,48] The second thermal decomposition step (temperature range: 210−580 °C, TG mass loss: ~63% (theory: 67.54%), three DTG peaks: ~285, 393, and 519 °C) is assigned as the decomposition of $Ca(CH_3CHOHCOO)_2$, eliminating $CH_3CHOHCOOC_2H_5$ and forming $CaCO_3$. However, the thermal elimination of $CH_3CHOHCOOC_2H_5$ is a complex process because of the presence of many DTG peaks.[49,50] This complex process is in good agreement with the thermal decomposition curve of $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ reported by Mititelu et al.[18] The final thermal decomposition
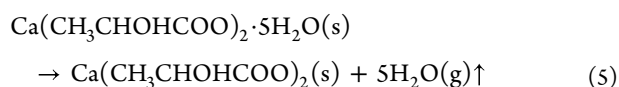
Figure 3. Thermal decomposition behaviors (TG/DTG curves) of calcium lactates (CL) prepared from cockle (CS, a, b), mussel (MS, c, d), and oyster (OS, e, f) shells using 6, 8, and 10 mol/L lactic acid.
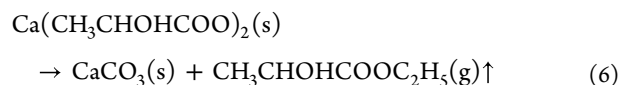

Figure 4. X-ray diffraction patterns of calcium lactates (CL) prepared from cockle (CS, a), mussel (MS, b), and oyster (OS, c) shells using 6, 8, and 10 mol/L lactic acid.

step (temperature range: 580–710 °C, TG mass loss: ~79% (theory: 81.81%), DTG peak: ~667 °C) is assigned as the decomposition of $CaCO_3$, eliminating CO_2 gas and forming CaO as a final product.[18] This CO_2 elimination process was called the "decarbonation process".[51] Therefore, considering the first, second, and third thermal decomposition steps, the decomposition mechanism of the synthesized Ca-$(CH_3CHOHCOO)_2 \cdot 5H_2O$ can be expressed using eqs 5–7:

Dehydration (30–210 °C):

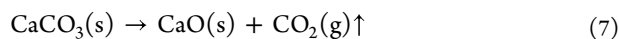$$Ca(CH_3CHOHCOO)_2 \cdot 5H_2O(s)$$
$$\rightarrow Ca(CH_3CHOHCOO)_2(s) + 5H_2O(g)\uparrow \quad (5)$$

Ethyl-lactate elimination (210–580 °C):

$$Ca(CH_3CHOHCOO)_2(s)$$
$$\rightarrow CaCO_3(s) + CH_3CHOHCOOC_2H_5(g)\uparrow \quad (6)$$

Decarbonization (580–710 °C):

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)\uparrow \quad (7)$$

3.5. Crystallography. An XRD was used to investigate the crystallography of all calcium lactate samples derived from different bivalve shells. The resulting diffractograms were then employed to confirm the chemical formula by comparing it to the international diffraction databases.[38] The diffraction patterns of calcium lactate samples prepared from the cockle, mussel, and oyster shells using three different lactic acid concentrations (6, 8, and 10 mol/L) are demonstrated in Figure 4a, b, and c, respectively. A slight difference in the
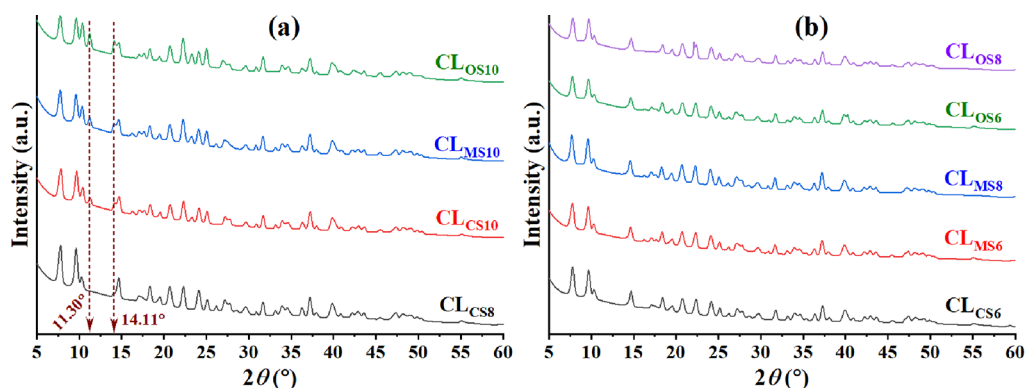
Figure 5. X-ray diffraction patterns of mixed DL- and L-enantiomers (a) and single L-enantiomer (b) of $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ derived from cockle (CS), mussel (MS), and oyster (OS) shells using 6, 8, and 10 mol/L lactic acid.
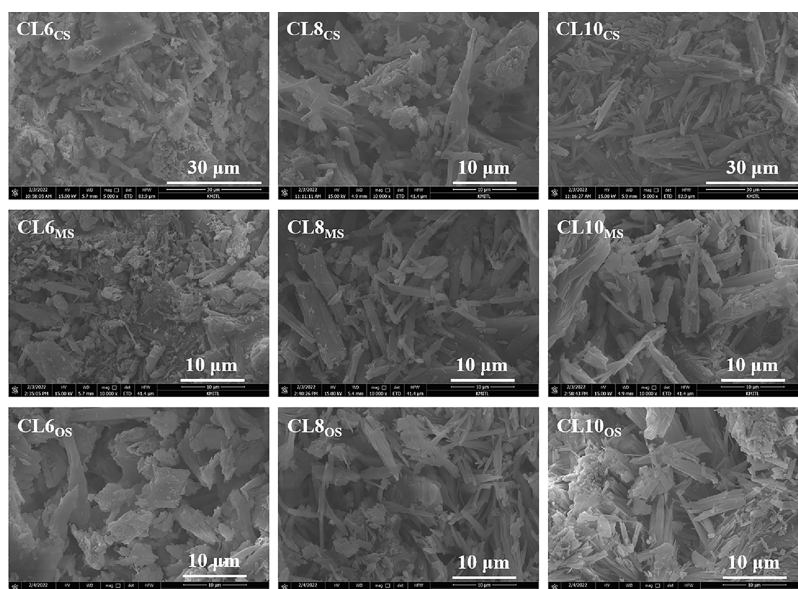
Figure 6. Scanning electron microscopic images of calcium lactates (CL) prepared from cockle (CS), mussel (MS), and oyster (OS) shells using 6, 8, and 10 mol/L lactic acid.

diffraction patterns was observed. According to the resulting diffractograms, the calcium sources have no impact on the crystallography of samples; however, the concentration of lactic acid can influence this sample characteristic. At high lactic acid concentrations (e.g., 8 and/or 10 mol/L), some different diffraction peaks such as at 2θ of 11.30 and 14.11° were observed. These observed diffraction peaks indicated the different characteristics of the crystallography (crystal structure) of the synthesized calcium lactate compounds. These different diffractograms of calcium lactate obtained in this work agree with the diffractograms reported in the previous work.

Tansman et al.[19] applied the X-ray diffraction technique to differentiate the enantiomeric phases of $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ crystals. They first generated the diffraction patterns from the crystals and then compared them with the reference pattern of known crystal form. After the analysis, they observed two slightly different diffraction patterns, pointing out that $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ has two different crystalline (enantiomeric) phases, namely, calcium L-lactate pentahydrate and calcium DL-lactate pentahydrate[18,19] based on the enantiomeric characteristic of lactate ($CH_3CHOHCOO^-$) anions (e.g., L- and D-enantiomeric

$CH_3CHOHCOO^-$) in the crystal structure of $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$.[19,52] "Calcium D-lactate pentahydrate" means that $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ contains two $CH_3CHOHCOO^-$ groups in the right-enantiomeric characteristic. On the other hand, "Calcium L-lactate pentahydrate" means that $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ contains two $CH_3CHOHCOO^-$ groups in the left-enantiomeric characteristic. In addition, mixed-enantiomeric forms of $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ between D- and L-$CH_3CHOHCOO^-$ in the crystal structure were also observed, which was called calcium DL-lactate pentahydrate.[19,55] The reference pattern of ICDD no. 00-029-1596 was assigned as the DL-enantiomeric form of $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$.[19,47]

Therefore, after comparing to the ICDD #00-029-1596 and the diffraction patterns reported by Tansman et al.,[19] the diffraction patterns were grouped as two groups based on the enantiomers of $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$. It can be concluded that the lowest and medium concentrations (6 and 8 mol/L) of lactic acid provided the $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ with the L-enantiomeric form whereas at the highest lactic acid concentration (10 mol/L), $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ with both DL- and L-enantio-

meric forms were observed. However, when the cockle-shell-derived $CaCO_3$ was reacted to the lactic acid with a concentration of 8 mol/L, both DL- and L-Ca-$(CH_3CHOHCOO)_2 \cdot 5H_2O$ crystals were also observed. Figure 5a,b demonstrates the diffraction patterns of mixed DL- and L-enantiomers and single L-enantiomer of Ca-$(CH_3CHOHCOO)_2 \cdot 5H_2O$ prepared from cockle (CS, a), mussel (MS, b), and oyster (OS, c) shells using 6, 8, and 10 mol/L lactic acid. All obtained diffraction patterns of calcium lactate crystals are in good agreement with the experimental results described in vibrational spectroscopic and TG results, which confirmed the presence of $CH_3CHOHCOO^-$, H_2O, and Ca–O functional groups and the mole number of H_2O (5 moles) that existed in the crystal structure of Ca-$(CH_3CHOHCOO)_2 \cdot 5H_2O$, respectively.

3.6. Morphology. An electron microscope was used to investigate the morphological characteristics of the bivalve-shell-derived calcium lactates prepared from different lactic acid concentrations (6, 8, and 10 mol/L). The morphologies of all samples are demonstrated in Figure 6. One of the superior properties of calcium lactate more than other calcium compounds is its good solubility, bioavailability, and non-toxicity.[18] Therefore, calcium lactates have been used as an anti-carcinogen,[53] a calcium supplement,[54] an anti-microbial,[55] etc. Recently, Mititelu et al.[18] synthesized calcium lactates by using Romanian Black Sea mussel shells as raw material and then used the synthesized calcium lactate as the immediate-release tablets. These obtained tablets were further applied in the pharmaceutical field as a calcium source for treating calcium deficiencies.

The crystal morphology engineering of the product is an effective tool for enhancing its pharmaceutical performance;[56] therefore, the crystal morphology engineering (shape and size) of the synthesized calcium lactate crystals was also investigated in this work. However, investigating the pharmaceutical performance of calcium lactate products derived from cockle, mussel, and oyster shells is recommended as future work. The microscopic results of all synthesized calcium lactates showed the same morphological characteristics. The firewood-like shape of different microsizes was mostly observed, together with irregular shapes due to the breakage phenomena of firewood-like particles, forming smaller irregular particles. The differences in calcium sources and lactic acid concentration strongly influence morphological characteristics. For example, the morphologies reported in this work are significantly different from those of calcium lactate produced from the scallop shells (a prism-like structure, together with islands) reported in our previous work.[18]

4. CONCLUSIONS

Bivalve-shell wastes were successfully employed as the renewable calcium source for the preparation of advanced material. Cockle, mussel, and oyster shells were cleaned and milled, obtaining a renewable calcium source ($CaCO_3$). The reaction between $CaCO_3$ and lactic acid generated a Ca^{2+}-$2CH_3CHOHCOO^-$-H_2O systematic solution. After the drying process, $Ca(CH_3CHOHCOO)_2 \cdot nH_2O$ crystals were formed. The vibrational results confirmed the presence of $CH_3CHOHCOO^-$, H_2O, and octahedral CaO_8. The TG profiles pointed out that the mole number of H_2O in the crystal structure of $Ca(CH_3CHOHCOO)_2$ is equal to 5, forming $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$, which can further be used in the pharmaceutical application. The highest solubility

was observed when the cockle-shell waste was used as a calcium source for the production of $Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$. Triple thermal decomposition steps of Ca-$(CH_3CHOHCOO)_2 \cdot 5H_2O$ were observed under high-temperature conditions, and the final decomposition product was CaO. The concentration of lactic acid can influence the crystallography of products. The diffraction patterns of the products demonstrated that using low acidic concentrations (6 and 8 mol/L), an enantiomeric L-$Ca(CH_3CHOHCOO)_2 \cdot 5H_2O$ was observed. In contrast, both L- and DL-Ca-$(CH_3CHOHCOO)_2 \cdot 5H_2O$ enantiomers were formed when a high acidic concentration (10 mol/L) was used in the preparation process. The microscopic results exhibited that the morphological characteristics of products mostly consisted of firewood-like shapes in different microsizes. In summary, this research provided an effective, green, simple, and low-cost preparation of value-added calcium lactate by using biowaste-based material as a raw starting agent, which helps the reduction of CO_2 emissions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c02042.

> Process line of production for the Bio-green CaCO3 powder obtained from bivalve shell wastes; calculation of carbon emissions in the production of the Bio-green $CaCO_3$ powder obtained from bivalve shell wastes; experimental percentages of the mass loss and residual mass of calcium lactates (CL) prepared from cockle (CS), mussel (MS), and oyster (OS) shells using 6, 8, and 10 mol/L lactic acid (PDF)

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Notes
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