TECHNICAL NOTE

Thermal properties of 3-hydroxy fatty acids and their binary mixtures as phase change energy storage materials

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Summary
In the present work, we describe the chemical synthesis of 3-HFAs as prominent derivatives of fatty acids and assess if they could be applied as phase change materials (PCM). In addition, 3-HFAs were obtained by depolymerization of a bacterial biopolymeric material, polyhydroxyalkanoate. Thermal properties of 3-hydoxyoctanoic, decanoic, and dodecanoic acids are reported for the first time. These materials showed the potential to be applied as PCM in temperature range from 33°C to 66°C. In order to expand the temperature range for application of 3-HFAs as PCM, eutectic mass ratios of three kinds of binary mixtures of 3-HFAs were calculated, and their properties were predicted using the Schröder-van Laar equation. Thermal properties of these mixtures were validated by differential scanning calorimetry (DSC) analysis. These results showed that eutectics considerably expanded the scope of applications of 3-HFAs as PCMs. 3-HFAs originating from biotechnologically obtained polyhydroxyalkanoates also showed potential to be applied in development of PCMs.

KEYWORDS
3-hydroxy fatty acids, biopolymer, eutectic mixtures, phase change materials, thermophysical properties

1 | INTRODUCTION

Phase change materials (PCMs) absorb or release large amount of latent heat when they change their physical state, usually a solid-liquid phase transition. This property makes them suitable for thermal energy storage applications. In order for a material to be considered as PCM, several properties should be evaluated: thermal,

Abbreviations: PCM, phase change material; PHA, polyhydroxyalkanoate; FA, fatty acid; 3-HFA, 3-hydroxy fatty acid; DSC, differential scanning calorimetry

physical, kinetic, chemical, and economic.[1] Desirable properties of PCMs are appropriate transition temperature, large enthalpy change at the transitions, good chemical stability over many cycles, low toxicity, non-corrosiveness, no fire hazard, little supercooling, melt congruently, and low cost.[2-6]

There are a number of compounds that qualify as PCMs including both inorganic and organic materials.[7] Fatty acids (FAs) are the most studied and utilized for this purpose.[3,8] Pure FAs show excellent PCM qualities and have the advantage of being produced from renewable resources.[9] It has been reported that, two or more FAs can be mixed to form an eutectic mixture with a lower phase change temperature than any constituent in the mixture.[10,11] Number of FAs eutectic mixtures has been reported as suitable for cooling applications, such as in personal active cooling garments.[12,13] The critical characteristics of the eutectic mixture such as mass ratio, phase change temperature, and latent heat are obtained via the DSC analysis. These properties could be also predicted and calculated using the Schroder-Van Laar equation thus avoiding many time and resource consuming experiments.[14-17]

Derivatives of FAs, except unsaturated acids (oleic, linoleic) and different alkyl esters, have not been tested or used as PCMs. As prominent derivatives of FAs that could be applied as PCMs, we chose 3-hydroxyfatty acids (3-HFAs). These materials were obtained by the hydrolysis of polyhydroxyalkanoates (PHAs). PHAs are biodegradable polymers and can be made from renewable and even waste feedstocks by microorganisms.[18-20] If we regard FAs prepared from fats and oils as renewable sources, 3-HFAs can also be assumed as biobased renewable sources of PCMs. Also, 3-HFAs could be prepared by chemical synthesis using Reformatsky reaction.[21,22]

This study aimed at facile chemical and synthesis of a range of 3-HFAs from the biopolymers and investigation of their thermal properties. In addition, determination of their eutectic ratio has been undertaken. Consequently, they were evaluated as PCMs for storage and retrieval of thermal energy.

2 | MATERIALS AND METHODS

2.1 | 3-HFAs synthesis and spectral characterization

2.1.1 | Chemical synthesis and analysis of 3-HFA

All chromatographic separations were performed on Silica, 10–18, 60 Å, ICN Biomedicals. Standard techniques were used for the purification of reagents and solvents. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance at 500 MHz, (^{1}H at 500 MHz, ^{13}C at 125 MHz). Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hz. Tetramethylsilane was used as an internal standard. The following abbreviations were used for signal multiplicities (br s = broad singlet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets). IR spectra (ATR) were recorded with a Perkin-Elmer-FT-IR 1725X spectrophotometer; ν values are given in cm^{-1}. Melting points were determined on the Electrothermal WRS1B apparatus and were reported uncorrected.

a. Synthesis of ethyl-3-hydroxylakanoate by Reformatsky reaction

Into a refluxing suspension of activated zinc dust (1.52 g, 23.2 mmol) and anhydrous benzene (7 mL), a mixture of aldehyde (21.9 mmol) and ethyl bromoacetate (3.88 g, 23.2 mmol) in benzene (40 mL) was added during 1 hour. The mixture was stirred for an additional 1 hour at the same temperature (oil bath at 80°C), and then the mixture was cooled to 0°C. Then, a solution of 1 M HCl (1 mL) was added, and the reaction mixture was extracted with diethyl ether (3 × 25 mL). The combined organic solutions were dried over anhydrous Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The crude product was purified under reduced pressure on a silica gel column, with mixture of petroleum ether and ethyl acetate from 95/5 to 9/1 as eluent, to give the desired β-hydroxy ester.

Ethyl-3-hydroxyoctanoate was prepared starting from n-hexanal (2.19 g, 21.9 mmol) according to the described procedure as a colorless oil (yield: 2.63 g, 64%).
[1]**H NMR (500 MHz, CDCl$_3$):** δ_H 4.17 (2H, q, J = 7.1 Hz), 4.03 to 3.97 (1H, m), 2.97 (1H, br s), 2.50 (1H, dd, J_1 = 16.4 Hz, J_2 = 3.1 Hz), 2.40 (1H, dd, J_1 = 16.4 Hz, J_2 = 9.1 Hz), 1.56 to 1.25 (11H, m), 0.89 (3H, t, J = 6.9 Hz). [13]**C NMR (125 MHz, CDCl$_3$):** δ_C 172.8; 67.7; 60.3; 41.0; 36.1; 31.3; 24.8; 22.2; 13.8; 13.6. **IR (ATR):** 3453, 2931, 1734, 1374, 1169, 1029, 726 cm^{-1}.

Ethyl-3-hydroxydecanoate was prepared starting from n-octanal (1.24 g, 9.7 mmol) according to the described procedure as a colorless oil (yield: 1.2 g, 57%).
[1]**H NMR (500 MHz, CDCl$_3$):** δ_H 4.17 (2H, q, J = 7.2 Hz), 4.02 to 3.97 (1H, m), 2.50 (1H, dd, J_1 = 16.4 Hz, J_2 = 3.1 Hz), 2.40 (1H, dd, J_1 = 16.4 Hz, J_2 = 9.1 Hz), 1.56 to 1.23 (15H, m), 0.88 (3H, t, J = 7.0 Hz). [13]**C NMR (125 MHz, CDCl$_3$):** δ_C 172.8; 67.7; 60.3; 41.0; 36.1; 31.4; 29.1; 28.8; 25.1; 22.3; 13.8; 13.7. **IR (ATR):** 3454, 2928, 1735 cm^{-1}.

Ethyl-3-hydroxydodecanoate was prepared starting from *n*-decanal (2.89 g, 18.5 mmol) according to the described procedure as a colorless oil (yield: 2.5 g, 55%).

^{1}H NMR (500 MHz, CDCl$_3$): δ_H 4.17 (2H, q, $J = 7.1$ Hz), 4.03 to 3.96 (1H, m), 2.95 (1H, br s), 2.50 (1H, dd, $J_1 = 16.4$ Hz, $J_2 = 3.1$ Hz), 2.40 (1H, dd, $J_1 = 16.4$ Hz, $J_2 = 9.1$ Hz), 1.55 to 1.22 (19H, m), 0.88 (3H, t, $J = 6.9$ Hz). **^{13}C NMR (125 MHz, CDCl$_3$):** δ_C 173.1; 68.0; 60.6; 41.3; 36.5; 31.9; 29.5; 29.3; 25.4; 22.6; 14.2; 14.1. **IR (ATR):** 3454, 2926, 1735, 722, 548 cm^{-1}.

b. Preparation of 3-HFAs by hydrolysis of ethyl esters

Hydrolysis of ethyl esters of 3-HFAs was performed with LiOH in the mixture of solvents (THF/MeOH/H$_2$O = 1/1/1). Into the solution of ethyl esters of 3-HFAs (5.3 mmol) and THF (30 mL) was added methanol (30 mL) and LiOH (30 mL of 2.5 M solution in water). The reaction mixture was stirred for 3 hours at room temperature, then solvents were evaporated under vacuum. The mixture was acidified to pH 2 using HCl, and 3-HFAs were extracted by ethyl acetate (3 × 30 mL). The solvents were evaporated under reduced pressure, and desired 3-HFAs were obtained.

3-Hydroxyoctanoic acid was prepared starting from ethyl-3-hydroxyoctanoate (1 g, 5.3 mmol) according to the described procedure (yield: 0.84 g, 99%). This substance is an oil at room temperature, and its melting point was determined by DSC analysis (33.3°C).

^{1}H NMR (500 MHz, CDCl$_3$): δ_H 6.64 (1H, br s), 4.07 to 4.01 (1H, m), 2.57 (1H, dd, $J_1 = 16.5$ Hz, $J_2 = 3.1$ Hz), 2.47 (1H, dd, $J_1 = 16.5$ Hz, $J_2 = 9.0$ Hz), 1.60 to 1.24 (8H, m), 0.89 (3H, t, $J = 6.8$ Hz). **^{13}C NMR (125 MHz, CDCl$_3$):** δ_C 179.4; 69.7; 42.6; 38.0; 33.2; 26.7; 24.1; 15.5. **IR (ATR):** 3536, 3050, 2925, 1682, 1440, 1233, 1079, 912, 873, 548 cm^{-1}.

3-Hydroxydecanoic acid was prepared starting from ethyl-3-hydroxydecanoate (0.80 g, 3.7 mmol) according to described procedure as a white solid (yield: 0.69 g, 99%, mp). The melting point of this substance was determined using Electrothermal WRS1B (mp = 53°C), and melting point determined by DSC analysis is 52.6°C.

^{1}H NMR (500 MHz, CDCl$_3$): δ_H 4.08 to 4.01 (1H, m), 2.57 (1H, dd, $J_1 = 16.5$ Hz, $J_2 = 3.1$ Hz), 2.48 (1H, dd, $J_1 = 16.5$ Hz, $J_2 = 9.0$ Hz), 1.59 to 1.22 (12H, m), 0.88 (3H, t, $J = 7.0$ Hz). **^{13}C NMR (125 MHz, CDCl$_3$):** δ_C 179.5; 69.7; 42.6; 38.0; 33.3; 31.0; 30.8; 27.0; 24.2; 15.6. **IR (ATR):** 3535, 3050, 2922, 2851, 1681, 1441, 1223, 913, 715, 551 cm^{-1}.

3-Hydroxydodecanoic acid was prepared starting from ethyl 3-hydroxydodecanoate (1.00 g, 4.1 mmol) according to described procedure as a white solid (yield: 0.81 g, 92%). The melting point of this substance determined by

apparatus Electrothermal WRS1B is 68°C, and melting point determined by DSC analysis is 66.5°C.

^{1}H NMR (500 MHz, CDCl$_3$): δ_H 4.09 to 4.01 (1H, m), 2.58 (1H, dd, $J_1 = 16.5$ Hz, $J_2 = 3.0$ Hz), 2.48 (1H, dd, $J_1 = 16.5$ Hz, $J_2 = 9.0$ Hz), 1.60 to 1.21 (16H, m), 0.88 (3H, t, $J = 6.9$ Hz). **^{13}C NMR (125 MHz, CDCl$_3$):** δ_C 178.2; 68.4; 41.2; 36.7; 32.1; 29.8; 29.7; 29.5; 25.7; 22.9; 14.3. **IR (ATR):** 3534, 3055, 2920, 2850, 1682, 1469, 1442, 1217, 867, 556 cm^{-1}.

2.1.2 | Depolymerization of biopolymer

Biopolymers were produced via fermentation using *Pseudomonas putida* strains by Bioplastech Ltd. using basic fermentation conditions as described previously.[23,24] Two different types of polyhydroxyalkanoates (PHA) were provided by Bioplastech Ltd (Dublin, Ireland). A polyhydroxyoctanoate (PHO) sample contained >95% 3-hydroxyoctanoic acid as the monomer, while polyhydroxyoctanoate-co-decanoate (PHOD) contained 3-hydroxyoctanoic and 3-hydroxydecanoic acids in a 60:40 ratio and a very small quantity of corresponding unsaturated acids. Both biopolymers appeared yellowish in color and were used without additional purification.

Depolymerization of both biopolymers and subsequent monomeric acid preparation was performed with an improved procedure in comparison to a previously reported method.[25] PHO and PHOD (1.0 g) were dissolved in the mixture of solvents (THF/MeOH = 1/1, 60 mL), and LiOH (30 mL of 2.5 M solution in water) was added to obtain 3-HFAs via hydrolysis under alkaline conditions. Reaction mixture was stirred for 3 hours at room temperature, and solvents were evaporated under vacuum. The mixture was dissolved in water (30 mL) and washed with diethyl ether (3 x 30 mL). The aqueous solution of lithium salts of 3-HFAs was acidified to pH 2 using HCl, and 3-HFAs were extracted by ethyl acetate (3 × 30 mL). The organic solution was dried over anhydrous Na$_2$SO$_4$, and the solvent was evaporated under vacuum. The isolated yield of 3-HFAs was between 90% and 95%. The identity of 3-HFAs was assessed by gas chromatography using an Agilent Technologies 7890A GC System (HP-5MS) coupled to a mass spectrometer 5975 inert XL EI/CI MSD.

2.2 | Thermal analysis

2.2.1 | Sample preparation

Pure 3-HFAs were used as independent samples and for the preparation of the following binary mixtures: C8/C10, C8/C12, and C10/C12. A series of mixtures

(200 mg), with varying mass proportions of 3-HFAs, were prepared by weighing appropriate amounts of each pure acid on a Mettler Toledo AT250 Balance (accuracy ±0.03 mg). Both components were gently mixed by pestle for 5 minutes and heated until melted then cooled spontaneously to room temperature. Mixtures were stored in closed glass vials until their thermal properties were measured.

2.2.2 | DSC analysis

A differential scanning calorimeter (DSC, Q1000, TA Instruments, New Castle, DE, USA) was used to perform DSC experiments. Three independent samples (1.3-1.7 mg) of every pure FA and each different binary mixture were taken and placed in aluminum hermetic pans, hermetically sealed by a TA Instruments blue Sample Encapsulating Press. An identical empty sealed hermetic aluminum pan is used as a reference. The samples were cooled from 20°C to 3°C, then equilibrated for 5 minutes and scanned to 70°C, with a controlled heating rate of 5°C/min, under a N_2 purge flow of 50 mL/min. Phase diagrams of binary mixtures were obtained from DSC results, and eutectic points, typically called their eutectic mass ratio and eutectic phase change temperature, were determined. Five heat-cool cycles were measured for each sample of a eutectic binary mixture. Each thermogram was analyzed by TA Advantage Universal analysis 2000 software, version 4.5A. The endothermic melting peaks were characterized by the onset temperature (T_{on}), peak temperature (T_p), and endset temperature (T_{end}) of and melting enthalpy (ΔHm). The exothermic crystallization peaks were characterized by the onset temperature (Tc_{on}), peak temperature (Tc_p), and endset temperature (Tc_{end}) of and crystallization enthalpy (ΔHc).

2.3 | Calculation of eutectic mass ratios and thermal properties

Theoretical prediction method for mass ratio determination was performed as described previously.[11,14,16,26] Briefly, mass ratios of eutectic mixtures were determined through the phase diagram applying Schröder-van Laar equation:
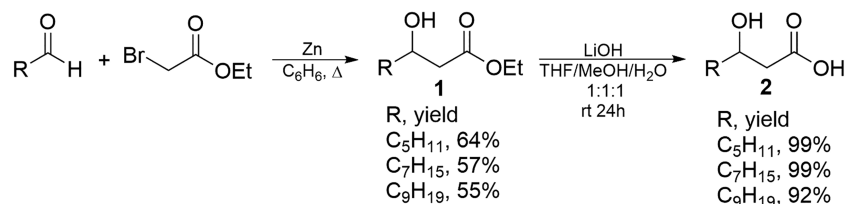
$$T_M = \left[\frac{1}{T_{O,A}} - R \cdot \frac{\ln X_A}{\Delta H_{m,A}}\right]^{-1}$$

$$T_M = \left[\frac{1}{T_{O,B}} - R \cdot \frac{\ln X_B}{\Delta H_{m,B}}\right]^{-1}$$

where T_M represents the melting temperature of the eutectic mixture in K, $T_{o,A}$ and $T_{o,B}$ represent the onset melting temperature in K, X_A and X_B represent the mole fraction, while $\Delta H_{m,A}$ and $\Delta H_{m,B}$ represent the molar latent heat in $J \cdot mol^{-1}$, of component A and B, respectively. R is the general gas constant ($8.314\ J \cdot mol^{-1} \cdot K^{-1}$).

The approach described by Yanping et al was used for the estimation of melting enthalpy of the 3-HFA eutectic mixture Hm,[14]:

$$H_m = T_m \sum_{i=1}^{n} \frac{X_i H_i}{T_i}$$

In this work, we used a computational tool developed and described by Kahwaji and White[17,27] which allowed us to add additional compounds to the data base.

3 | RESULTS AND DISCUSSION

3.1 | Preparation of 3-HFAs

One of the most efficient ways for the preparation of 3-HFAs is hydrolysis of appropriate ethyl esters, while Reformatsky reaction is one of the most useful methods for preparation of different 3-hydroxy esters (Scheme 1). Usually, Reformatsky reaction is performed with aldehydes and bromoesters in the presence of activated zinc in ethereal solution. Recently, Sailer et al described the preparation of ethyl esters of 3-hydroxy FAs in high yields, but in this procedure they used 2 equivalents of zinc and 2 equivalents of ethyl bromoacetate per one equivalent of aldehyde which made the atom economy of the reaction somewhat problematic.[22] Due to this reason, we decided to apply a modified procedure using benzene as a solvent.[28] The reaction was performed using nearly equimolar quantities of reactants in boiling solvents for 1 hour, and ethyl esters of 3-HFAs were prepared in 55% to 64% yields (Scheme 1). In the subsequent step, ethyl esters of 3-HFAs were hydrolyzed with LiOH in the ternary mixture of solvents THF,

SCHEME 1 Synthetic route for the preparation of 3-HFAs

MeOH, and H_2O in a volume ratio of 1:1:1, and 3-HFAs were isolated in nearly quantitative yields.

The hydrolysis of esters was improved in comparison to the published procedure.[22] As a model compound, we used ethyl ester of 3-hydroxyoctanoic acid. Firstly, potassium hydroxide was tested as a base in the mixture of solvents hexane/methanol (1/1), and the product was isolated with a yield of 80% (Table 1). Given that lithium hydroxide in the mixture of solvents THF/H_2O is known as an efficient hydrolyzing agent, we have assessed it on ethyl ester of 3-hydroxyoctanoic acid. However, these conditions were ineffective when applied on the model reaction. We concluded that the solubility of esters is the main problem and decided to apply a ternary mixture of $THF/MeOH/H_2O$ as a medium for hydrolysis. When the hydrolysis was performed in the mixture of these solvents in a ratio of 3:2:1 for 3 hours, at room temperature the expected product was isolated at 98%. Prolonging the reaction to 24 hours reduced the product yield to 92%. The best result was obtained when the reaction was performed in the mixture of solvents 1:1:1 at room temperature for 3 hours. 3-Hydroxyoctanoic acid was isolated at 99% yield, and this condition was applied for the preparation of other 3-HFAs. Similarly, this procedure has been applied for the hydrolysis of biotechnologically obtained PHA.

## 3.2 | Differential scanning analysis of pure 3-HFAs

Pure 3-HFAs obtained by Reformatsky reaction were analyzed using differential scanning calorimetry (DSC). Melting and crystallization DSC curves of individual 3-HFAs with 8, 10, and 12 carbon atoms are presented in Figure 1. The data obtained from DSC curves corresponding to the endothermal transition of melting: onset (T_{onset}), peak (T_{peak}) end temperature (T_{end}) of melting and enthalpies of melting (ΔH_m) and exothermal

TABLE 1 Hydrolysis of 3-hydroxyoctanoic acid ethyl ester

Base	Solvent(s)	Reaction Time, Temperature	Yield, %
KOH/MeOH	Hexane	1.5 h, reflux	80
LiOH (2.5 M in H_2O)	$THF/MeOH/H_2O$ 3/2/1, (rt)	24 h, rt	92
LiOH (2.5 M in H_2O)	THF/H_2O 2/1, (rt)	3 h, rt	No reaction
LiOH (2.5 M in H_2O)	$THF/MeOH/H_2O$ 3/2/1, (rt)	3 h, rt	98
LiOH (2.5 M in H_2O)	$THF/MeOH/H_2O$ 1/1/1, (rt)	3 h, rt	99

crystallization transition: onset (T_{onset}), peak (T_{peak}), end temperature (T_{end}), and enthalpies of crystallization (ΔH_c) of samples are summarized in Table 2.

Considering the melting temperatures (Table 2), 3-hydroxyoctanoic acid was melted in a temperature range of 33.3°C to 37.19°C, 3-hydroxydecanoic acid in the range of 52.62°C to 55.96°C, while the 3-hydroxydodecanoc acid is melted in a temperature range of 66.45°C to 69.89°C. The obtained value of the latent heat of melting (ΔH_m) of 3-hydroxyoctanoic acid is 126.1 Jg^{-1}, for the 3-hydroxydecanoic acid is 127.8 Jg^{-1}, while for the 3-hydroxydodecanoic acid the value is 157.3 Jg^{-1}. On the basis of the obtained data, it can be concluded that with the length of the hydrocarbon chain the values of the melting temperature and the latent heat of melting of the tested acids increased. Therefore, tested acids showed a temperature of melting (T_{onset}) from 33°C to 66°C and could be applied as PCM in this temperature range. (R)-3-Hydroxyoctanoic acid obtained by depolymerization of biotechnologically obtained PHO showed difference in thermal properties compared with chemically synthesized racemic mixture (Table 2). Considerably lower melting temperatures as well as lower value of the latent heat of melting (ΔH_m) could possibly be due to the presence of 8.5% (w/w) of unsaturated octanoic acid in the sample after described treatment of the polymer, as judged by GCMS analysis. Nevertheless (R)-3-hydroxyoctanoic acid obtained from the biopolymer can be considered as PCM after further purification step(s) as it has been recognized that the melting temperature is highly dependent on the purity of FAs.[8] One of the suitable methodologies would be to use activated charcoal during the
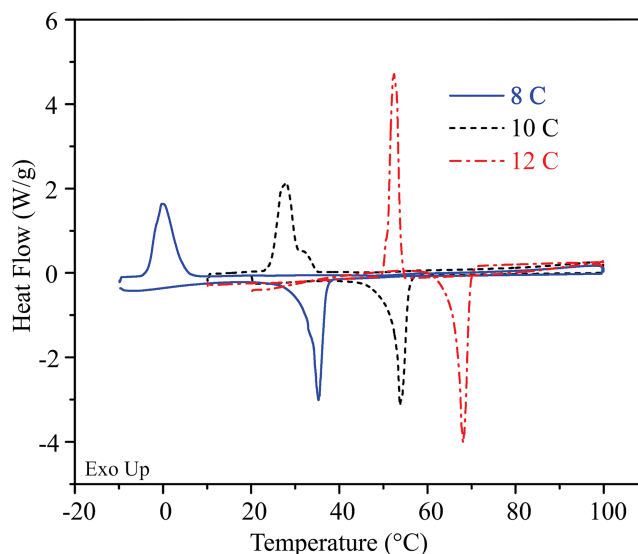
FIGURE 1 Differential scanning calorimetry (DSC) curves of individual 3-HFAs (8C—3-hydroxyoctanoic acid; 10C—3-hydroxydecanoic acid; 12C—3-hydroxydodecanoic acid) [Colour figure can be viewed at wileyonlinelibrary.com]

downstream processing of PHA itself.[29] Recently, (R)-3-hydroxynonanoic and (R)-3-hydroxyheptanoic acids from the PHA were successfully used in the preparations of new deep eutectic solvents with low toxicity.[30]

Thermal and chemical stability of pure 3-HFAs were tested using DSC method and ^{1}H NMR spectroscopy. As a model, we used 3-hydroxydodecanoic acid (Figure 2). Small variations in the melting temperature and the change in the latent heat of melting of each of the tested acids were observed, and it can be concluded that they are thermally stable, in cyclic heating and cooling, in the tested temperature range (Figure 2A). The DSC curves of the tested acids reveal that after each heating-cooling cycle, only one thermal transition with the same onset temperature is observed, indicating the thermal stability of the substances in the temperature range of −70°C to 70°C. The chemical stability of the tested acids was additionally confirmed by comparing the ^{1}H NMR spectra of acids before and after the thermal cycles (Figure 2B). By comparing the spectra, it has been established that there was no difference in chemical shifts and integrals before and after the thermal cycles (Figure 2B). This is the first study reporting the thermal properties of even chain 3-HFAs, and we show that these acids have higher melting temperatures than their corresponding FAs.[8] Similarly,

TABLE 3 Predicted and calculated properties of eutectic mixtures of 3-HFAs

| Mixtures 3-HFAs	Calculated Values			Experimental Data		
	χ	T_m, °C	ΔH_m, J g^{-1}	χ	T_m, °C	ΔH_m, J g^{-1}
C8-C10	0.60-0.40	16.04	119.21	0.70-0.30	6.60	47.68
C8-C12	0.74-0.26	24.33	128.43	0.90-0.10	9.12	2.57
C10-C12	0.63-0.37	36.63	127.13	0.60-0.40	42.57	108.23

melting temperatures of 3-hydroxyheptanoic and 3-hydroxynonanoic acid were reported with the similar trend observed.[30]

## 3.3 | Determination of eutectic composition of binary mixtures of 3-HFAs

In order for the PCM to be used for thermal energy storage, their melting temperature should match the temperature at which energy should be stored or released. Often, a PCM composed of a specific FA with a specific melting temperature does not exist, and in such cases eutectic mixture can help to expand their phase change

TABLE 2 Thermal properties of 3-hydroxyfatty acids (3-HFAs)

3-HFA	Melting				Crystallization			
	T_{onsetv}, °C	T_{peak}, °C	T_{end}, °C	ΔH_m, J g^{-1}	T_{onset}, °C	T_{peak}, °C	T_{end}, °C	ΔH_c, J g^{-1}
3-Hydroxyoctanoic acid	33.30	35.28	37.19	126.12	1.33	−2.41	−7.11	99.56
3-Hydroxydecanoic acid	52.62	53.73	55.96	127.81	34.04	30.47	27.86	132.00
3-Hydroxydodecanoic acid	66.45	68.07	69.89	157.32	53.97	52.44	49.94	153.97
(R)-3-Hydroxyoctanoic acid	−1.64	10.38	12.37	43.01	−40.03	−35.30	−32.32	54.40
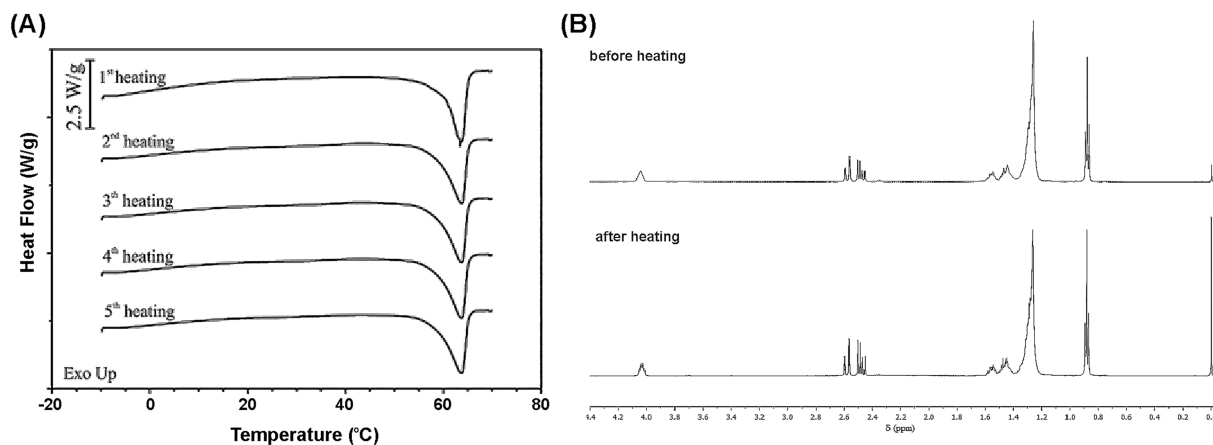
FIGURE 2 (A) Differential scanning calorimetry (DSC) curves of 3-hydroxydodecanoic acid heating-cooling cycles; (B) 1H NMR spectrum of 3-hydroxydodecanoic acid (A) before and (B) after the application of five heating-cooling cycles
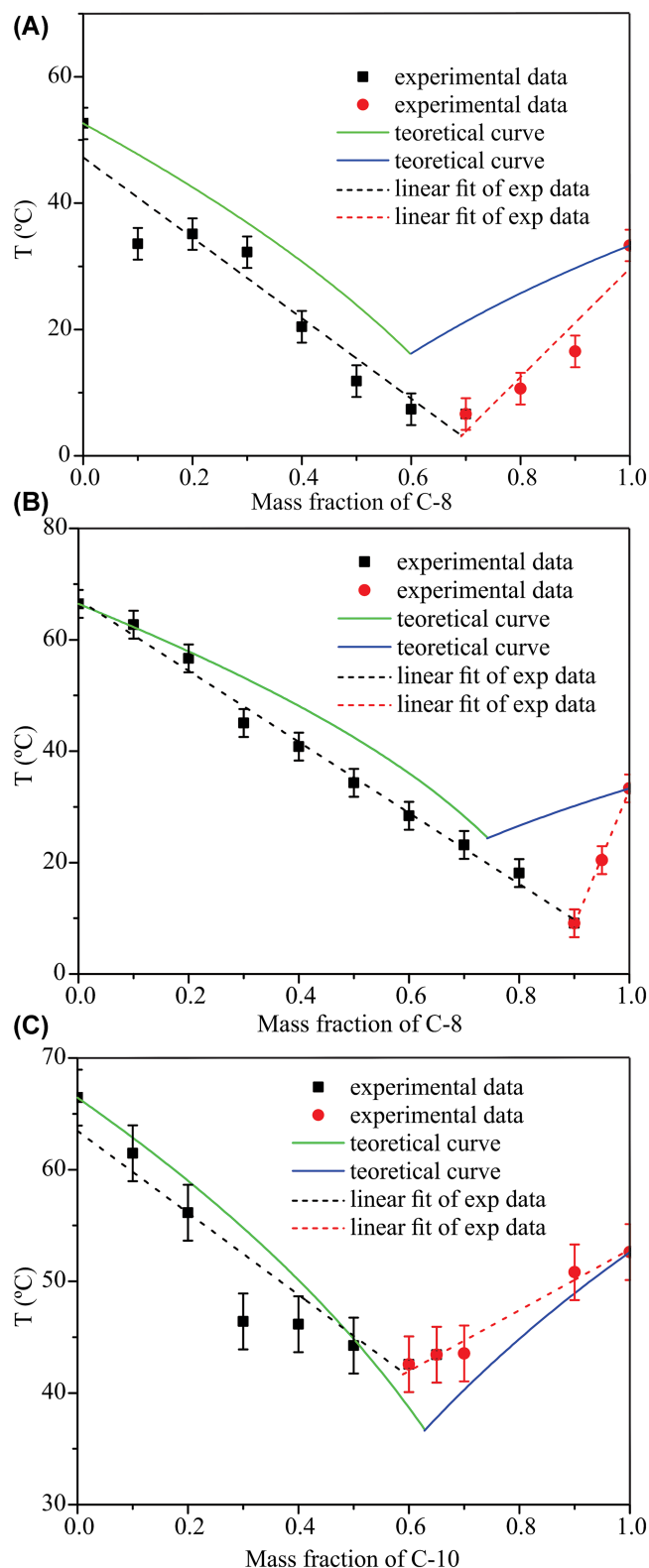
FIGURE 3 Phase diagrams of 3-HFAs binary mixtures: (A) C8/C10; (B) C8/C12; (C) C10/C12 (C8—3-hydroxyoctanoic acid; C10—3-hydroxydecanoic acid; C12—3-hydroxydodecanoic acid) [Colour figure can be viewed at wileyonlinelibrary.com]

temperature range.[16,17,31] Given that synthetically obtained 3-HFAs showed temperatures of melting (T_{onset}) from 33°C to 66°C (Table 2), the thermal properties of the following acid mixtures were examined: (a) 3-hydroxyoctanoic and 3-hydroxydecanoic acid (C8-C10), (b) 3-hydroxyoctanoic and 3-hydroxydodecanoic acid (C8-C12), and (c) 3-hydroxydecanoic and 3-hydroxydodecanoic acid (C10-C12) (Table 3).

Firstly, using the Schröder-van Laar equation, applying the model described by Kahwaji and White,[17] and experimental data for chemically obtained pure 3-HFAs (Table 2), we predicted the ideal mass ratio of eutectic mixtures of C8-C10, C8-C12, and C10-C12, as well as their thermal properties (Table 3, Figure 3). Following this, an experimental validation of the predicted values for eutectic mixtures was carried out (Table 3). Notably, the significant disagreement between predicted and experimental values was observed for C8-C12 mixture, with ΔH_m value being 2.57 J g^{-1} instead of calculated 24.33 J g^{-1}. In this case, it can be proposed that the peritectic mixture was formed as in case of certain FAs.[32] Phase diagrams of binary mixtures provide evidence that experimentally obtained results are in generally good agreement with the predicted data (Figure 3). The melting temperatures of these eutectics extended the temperature range of these materials and thus increased their application potential. A similar approach has successfully been used with FAs covering the melting temperature range from 15°C to >50°C.[16,33] Recently, binary mixtures of fatty alcohols and FA esters with chain length ≥ C12 were derived and suggested to be suitable as PCMs for building application.[34] Phase change properties of the sample derived from biopolymeric material, PHOD, containing preset amounts of 3-HFAs (C8 and C10) has been assessed by DSC showing no clear transition peaks (data not shown). This could be due to the fact that 3-HFAs mixture obtained from this biopolymer was not simple binary mixture but contained at least two other major components, namely unsaturated and saturated C8 and C10 acids in 16% to 25% (w/w) and 4% to 6% (w/w), respectively. Therefore, when considering biopolymer as a source of PCM, its purity, initial monomeric composition, as well as depolymerization procedure, should be taken into account.

4 | CONCLUSION

In summary, thermal properties of 3-hydroxyoctanoic, 3-hydroxydecanoic, and 3-hydroxydodecanoic acids have been determined by DSC. Their PCM properties have been extended by preparation of their binary eutectic mixtures. The melting peak temperatures of selected 3-HFAs

and their mixtures were between 16°C and 66°C deemed as suitable for personal active cooling garments. Importantly, 3-HFAs from biotechnologically obtained polyhydroxyalkanoates showed potential to be used as a source of PCMs providing the improved hydrolysis of the biopolymer, as well as purification procedure. This study highlights the possibility to further extend the application of biodegradable and biocompatible materials, such as PHA, in the field of thermal energy storage and retrieval.

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