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Article

Effect of Mixing Erythritol and Its Fluorine Analogues to Suppress Supercooling

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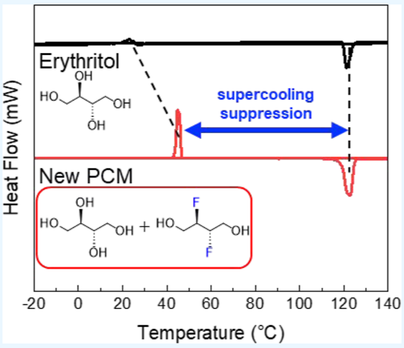
ABSTRACT: Erythritol is a latent heat storage material suitable for the utilization of unused heat in the medium temperature range of 100−250 °C. However, the supercooling characteristic of sugar alcohols reduces the energy utilization efficiency. In this study, erythritol and its fluorine analogues are mixed to suppress supercooling. Erythritol mixed with 2,3-difluorobutane-1,4-diol at a weight ratio of 1% is determined to be effective in suppressing supercooling. This indicates the possibility of utilizing energy more efficiently.



1. INTRODUCTION

In recent years, energy issues, such as fossil fuel depletion and rising carbon dioxide emissions, have garnered significant attention, driving momentum toward energy conservation. Thermal storage technology, which recaptures and reutilizes unused thermal energy, contributes to energy conservation. There are three primary types of thermal storage: sensible, chemical, and latent. Among these, latent heat storage stands out as a particularly promising method due to its high energy storage density and ability to retain heat at a constant temperature corresponding to the phase transition temperature of phase change materials (PCMs).[1] However, phase-change materials present challenges such as thermal conductivity[2,3] and supercooling,[4,5] which hinder their practical application.

The majority of industrial waste heat registers below 250 °C,[6,7] making erythritol a viable candidate for use within this temperature range. With a melting point of approximately 120 °C and a latent heat capacity ranging from 300 to 355 kJ/kg,[8−11] erythritol boasts a high capacity for an organic substance, attracting considerable research interest as a potential PCM.[12] Moreover, erythritol doubles as a sweetener[13] with established safety credentials. However, sugar alcohols like erythritol exhibit significant supercooling,[3,4] substantially diminishing energy utilization efficiency. Supercooling degree is influenced by factors such as material quantity, container properties, and environmental conditions (e.g., motionless or dynamic), all impacting crystal nucleation. While the mechanism of supercooling remains elusive, it is believed to stem from inadequate nucleation and slow crystal growth rates.[14−16] Consequently, one approach to mitigating supercooling involves incorporating other substances as nucleating agents, with research exploring various candidates.[16−20] Nonetheless, the disparity in specific gravity between the latent heat storage material and the added nucleating agent may precipitate phase separation over prolonged usage. Moreover, many nucleating agents under investigation are solids, yet achieving a homogeneous system (liquid phase) is preferable to prevent potential pipe blockages when integrated into a distribution system alongside erythritol. To address these challenges, we turned our attention to fluorine analogues of erythritol, where fluorine replaces the hydroxy group. Initially, fluorine shares similar characteristics with the hydroxy group, including the ability to form hydrogen bonds and comparable size.[21] Additionally, fluorine analogues exhibit anticipated properties such as a similar melting point to erythritol[22] and no phase separation when combined with erythritol. Given these shared traits with erythritol, we hypothesized that fluorine analogues might possess latent heat storage material properties. Furthermore, we speculated that blending fluorine analogues with erythritol could suppress supercooling by altering intermolecular interactions, effectively resolving issues related to phase separation and pipe blockage. While numerous studies have explored mixing solid particles as nucleating agents, limited research has investigated supercooling suppression through mixing with PCM of similar structure. Thus, our study aims to synthesize a fluorine

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analogue of erythritol and examine its latent heat properties when combined with erythritol.

2. MATERIAL AND METHODS

The structural formula of the substances used in this experiment is shown in Figure 1.

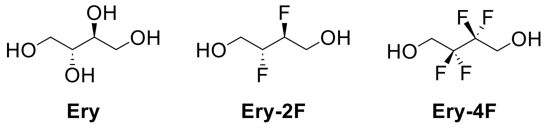

Figure 1. Structural formula of the substances used in this experiment.

Erythritol (>99.0%, abbreviated as "**Ery**" hereafter) was purchased from Tokyo Chemical Industry. 2,3-Difluorobutane-1,4-diol (abbreviated as "**Ery-2F**" hereafter), a fluorine analogue of erythritol (**Ery**), was synthesized following a previous study.[22,23] The detailed synthesis method is outlined in the Supporting Information (Figure S1). 2,2,3,3-Tetrafluoro-1,4-butanediol (abbreviated as "**Ery-4F**" hereafter) was purchased from Sigma-Aldrich Co. **Ery-4F** was utilized to investigate the impact of the number of fluorine atoms compared to **Ery-2F**. Differential scanning calorimetry (DSC) (Thermo Plus EVO2 DSCvesta, Rigaku Corp.) was employed to examine the latent heat properties of mixtures of **Ery-2F** with **Ery** and **Ery-4F** with **Ery**. Mixtures were prepared by physically mixing for 5 min using a mortar and pestle to ensure consistency between samples. Mixed samples were prepared by varying the weight ratio. Approximately 2 mg of sample was placed in a φ 5 mm × 2.5 mm aluminum pan, covered with a φ 4.5 mm aluminum lid, and analyzed under a 50 mL/min N_2 flow. Data collection was conducted between −20 and 140 °C, with both heating and cooling rates set at 5 °C/min.

3. RESULTS AND DISCUSSION

3.1. Erythritol and 2,3-Difluorobutane-1,4-diol.

Figure 2 illustrates DSC data measured for three cycles for a sample mixture of **Ery** and **Ery-2F**. The thermal properties derived from the DSC analysis are presented in Table 1. Table 1 includes the melting point (T_m), crystallization temperature (T_c), enthalpy of melting (ΔH_m), enthalpy of crystallization (ΔH_c), degree of supercooling (ΔT_s), and thermal utilization efficiency (eff) for each mixing ratio obtained from DSC. ΔT_s was calculated using the formula $\Delta T_s = T_m - T_c$ (°C). The thermal utilization efficiency is then briefly explained. During supercooled state, the stored thermal energy is dissipated as sensible heat. According to the law of conservation of energy, the more severe the supercooling phenomenon, the more thermal energy will be released in the form of sensible heat, which cannot be effectively utilized, resulting in a subsequent reduction in the amount of thermal energy that is released as latent heat. This explains the different melting and crystallization enthalpy values of the PCM. The ratio between the two values can be used to calculate the thermal utilization efficiency in the form of latent heat. The thermal utilization efficiency (eff) can be calculated using eq 1

$$\text{eff} = \Delta H_c / \Delta H_m \tag{1}$$

where ΔH_m and ΔH_c are the melting and crystallization enthalpy of samples, respectively, which can be obtained by DSC measurement.[20]

Figure 2a shows the DSC data for the samples mixed with **Ery** and **Ery-2F** at ratios of 100:0, 75:25, 50:50, 25:75, and 0:100. As shown in Table 1, the mixtures resulted in lower melting points than either **Ery** or **Ery-2F** as pure substances. This is thought to be due to the melting point depression. Conversely, with regard to the freezing point, the crystallization temperature peaks were clearly visible for both pure substances. However, in the mixture, the crystallization temperature was lower than that of the pure substances, suggesting increased difficulty in solidification. While the pure sample of **Ery-2F** showed a tendency to exhibit less supercooling than **Ery**, it resulted in a notably lower enthalpy of crystallization. Additionally, the enthalpy amount decreased after repeated cycles, indicating possible release of **Ery-2F** from the system rather than decomposition or alteration, confirmed by mass loss observed in the TG−DTA analysis (Figure S2).

As illustrated in Figure S2, **Ery-2F** showcased an endothermic peak at approximately 100 °C, accompanied by sample weight loss during heating to 140 °C. This result indicates the potential vaporization or thermal decomposition of **Ery-2F** during the DSC measurements, implying the slight alteration of the sample composition of the **Ery** and **Ery-2F** mixture during the DSC measurement cycle. Subsequently, to maintain the enthalpy amount of **Ery** as much as possible and mitigate supercooling, mixing ratios of **Ery** and **Ery-2F** were tested at 99.5:0.5, 99:1, 95:5, and 90:10 (Figure 2b). Table 1 reveals that the crystallization temperatures remained relatively

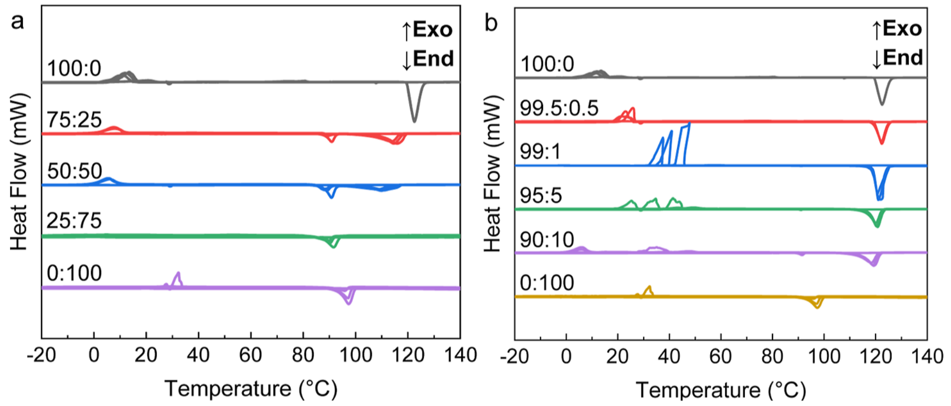

Figure 2. (a) Differential scanning calorimetry (DSC) data at mixing ratios of **Ery**/**Ery-2F** = 100:0, 75:25, 50:50, 25:75, 0:100. (b) DSC data at mixing ratios of **Ery**/**Ery-2F** = 100:0, 99.5:0.5, 99:1, 95:5, 90:10, 0:100.

Table 1. Thermal Properties of Erythritol (Ery) with 2,3-Difluorobutane-1,4-diol (Ery-2F)

Ery/Ery-2F	cycle number	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	ΔT_s (°C)	eff (%)
100:0	1	122.5	297	13.4	125	109.1	42.1
	2	122.5	294	10.0	119	112.5	40.5
	3	122.5	294	11.9	124	110.6	42.2
99.5:0.5	1	122.2	278	22.9	152	99.3	54.7
	2	121.4	266	21.5	150	99.9	56.4
	3	122.4	285	25.8	162	96.6	56.8
99:1	1	121.0	319	37.3	204	83.7	63.9
	2	121.0	327	47.7	224	73.3	68.5
	3	121.0	327	40.8	208	80.2	63.6
95:5	1	115.9, 120	8.18, 198	41.4	145	-[a]	70.3
	2	120.4	211	34.7	133	85.7	63.0
	3	120.8	212	25.4	124	95.4	58.6
90:10	1	91.5, 118.2	21.9, 195	35.1	150	[a]	69.1
	2	92.5, 118.9	2.36, 210	15.3, 5.9	42.0, 49.2	[a]	42.5
	3	119.3	219	8.8, 5.9	9.54, 90.7	113.4	41.6
75:25	1	90.9, 113.6	50.7, 137	16.4, 7.9	26.6, 63.5	[a]	47.9
	2	89.2, 114.7	19.4, 150	16.7, 7.6	7.89, 80.1	[a]	47.4
	3	89.6, 115.9	10.7, 157	14.8, 7.7	6.22, 77.4	[a]	49.8
50:50	1	90.8, 108.1	92.3, 87.5	5.3	96.6	[a]	53.7
	2	89.1, 109.9	51.7, 112	5.6	93.7	[a]	57.1
	3	88.3, 111	36.1, 122	6.1	81.5	[a]	51.6
25:75	1	91.6	132	12.6	54.6	79	41.4
	2	90.4	81.1	10.7	29.6	79.7	36.5
	3	89.9	55.7	5.2	10.0	84.7	18.0
0:100	1	97.4	163	32.3	78.1	65.1	47.9
	2	97.1	102	27.7	27.6	69.4	27.5
	3	95.8	34.4	19.7	2.42	76.1	7.06

[a] ΔT_s not calculated due to multiple peaks. T_m: melting point, T_c: crystallization temperature, ΔH_m: enthalpy of melting, ΔH_c: enthalpy of crystallization, ΔT_s: degree of supercooling, eff: thermal utilization efficiency.

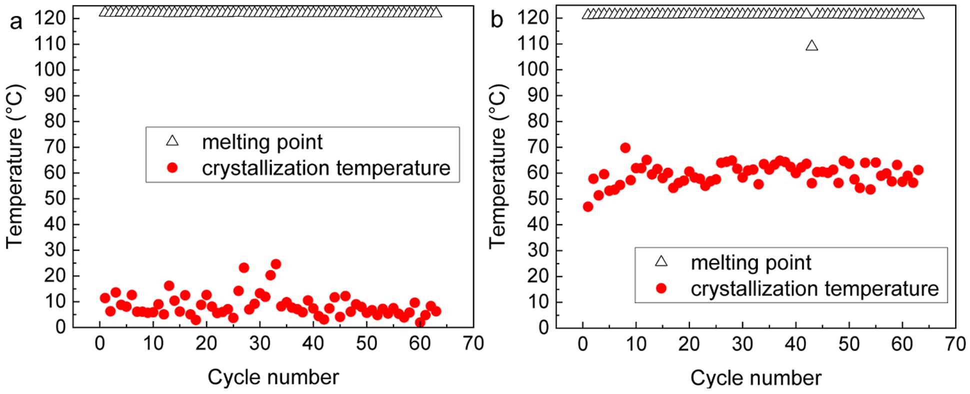

Figure 3. (a) Melting point and crystallization temperature of pure erythritol in each cycle. (b) Melting point and crystallization temperature for **Ery/Ery-2F** = 99:1 sample at each cycle.

consistent except for the second and third cycle of **Ery/Ery-2F** = 90:10. The presence of multiple crystallization temperatures observed for **Ery/Ery-2F** = 90:10 and 75:25 ratios could suggest separate crystallization of **Ery** and **Ery-2F** or differences in polymorphisms, as observed in D-mannitol,[19] necessitating further investigation. On the contrary, the degree of supercooling decreased in the first cycle for all mixing ratios. Particularly noteworthy was the mixture ratio of **Ery/Ery-2F** = 99:1, which exhibited an average supercooling degree of 79.1 and 31.7 °C lower than that of pure erythritol (**Ery**). This reduction in supercooling may be attributed to the minor addition of **Ery-2F** altering intermolecular interactions dominant in crystal nucleation. Regarding thermal utilization efficiency, except for the **Ery/Ery-2F** = 50:50 ratio, heat utilization efficiency tended to increase with decreasing amounts of added **Ery-2F**. However, the **Ery/Ery-2F** = 99:1 ratio showed higher thermal utilization efficiency compared to the **Ery/Ery-2F** = 99.5:0.5 ratio. This suggests that even a small amount of **Ery-2F** effectively suppresses supercooling, allowing efficient extraction of latent thermal energy inherent in **Ery**. Among these, the **Ery/Ery-2F** = 99:1 ratio stands out as the most effective in suppressing **Ery** supercooling, offering higher thermal utilization efficiency while addressing the supercooling issue, thus making it a promising PCM.

Table 2. Average of 63 Cycles of Measurements of Pure Erythritol and Ery/Ery-2F = 99:1

sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	ΔT_s (°C)	eff (%)
Ery	122.1 ± 0.082	277 ± 4.7	8.47 ± 4.4	94.6 ± 14	114 ± 4.4	34.0 ± 5.0
99:1	121.2 ± 1.5	286 ± 18	59.7 ± 4.0	213 ± 14	61.6 ± 4.1	74.4 ± 1.6

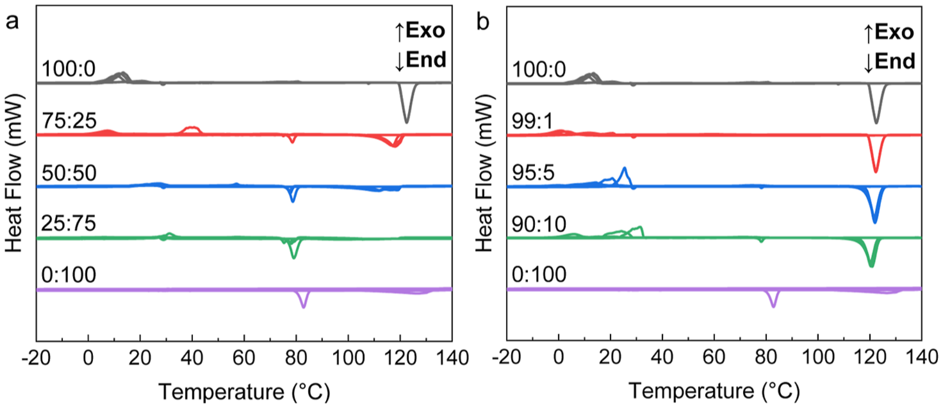

Figure 4. (a) Differential scanning calorimetry (DSC) data at mixing ratios of **Ery/Ery-4F** = 100:0, 75:25, 50:50, 25:75, 0:100. (b) DSC data at mixing ratios of **Ery/Ery-4F** = 100:0, 99:1, 95:5, 90:10, 0:100.

Table 3. Thermal Properties of Erythritol (Ery) with 2,2,3,3-Tetrafluoro-1,4-butanediol (Ery-4F)

Ery/Ery-4F	cycle number	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	ΔT_s (°C)	eff (%)
100:0	1	122.5	297	13.4	125	109.1	42.1
	2	122.5	294	10	119	112.5	40.5
	3	122.5	294	11.9	124	110.6	42.2
99:1	1	122.3	271	20.8, 2.9	74.4, 63.3	[a]	50.9
	2	122.3	271	10.4, 1.6	57.3, 77.2	[a]	49.8
	3	122.2	270	4.2, 0.8	32.5, 90.3	[a]	45.6
95:5	1	78.2, 121.7	5.44, 247	25.5	143	[a]	56.5
	2	122	256	20.7	116	101.3	45.3
	3	122	263	14.3	81.1	107.7	30.8
90:10	1	78.2, 120.2	14.1, 214	15.5, 5.9	35.1, 43.7	[a]	34.6
	2	120.5	227	24.2	121	96.3	53.3
	3	120.9	230	31.5	134	89.4	58.3
75:25	1	78.5, 116.9	34.2, 154	40.8	120	[a]	63.8
	2	75.1, 117.5	10.5, 127	16.6, 7.5	18.3, 47.8	[a]	42.1
	3	118	155	17.6, 6.7	51.1, 15.5	[a]	43.0
50:50	1	78.7, 110.9	87.3, 128	27	75.1	[a]	34.9
	2	77.7, 111.8	36.4, 112	24.5	60.6	[a]	40.7
	3	77.4, 118.6	22.1, 115	24	68.7	[a]	50.1
25:75	1	79.1, 97.6	125, 38.9	31.3	65.8	[a]	40.1
	2	78.0, 120.0	58.8, 37.1	28.5	40.9	[a]	42.6
	3	77.6, 108.9	33.8, 41.7	25	21.5	[a]	28.5
0:100	1	82.9	106	[b]	[b]		
	2	[b]	[b]	[b]	[b]		
	3	[b]	[b]	[b]	[b]		

[a] ΔT_s not calculated due to multiple crystallization peaks. [b] No clear peak was observed. T_m: melting point, T_c: crystallization temperature, ΔH_m: enthalpy of melting, ΔH_c: enthalpy of crystallization, ΔT_s: degree of supercooling, eff: thermal utilization efficiency.

A summarized graph of the two graphs shown in Figure 2 is shown in Supporting Information for easy comparison (Figure S3).

3.2. Range of Crystallization Temperature.

As mentioned earlier, it was observed that incorporating a small amount of **Ery-2F** effectively suppressed supercooling. However, it is essential to examine the stability and consistency of crystallization temperatures. Thus, differential scanning calorimetry (DSC) was conducted on a sample with a mixing ratio of **Ery/Ery-2F** = 99:1, which exhibited the most significant inhibition of supercooling, by increasing the number of heating cycles to 63. For comparison, Figure 3a illustrates the melting point and crystallization temperature of pure erythritol, while Figure 3b depicts the same for **Ery/Ery-2F** = 99:1. Table 2 presents the average values and standard deviations of the thermal properties obtained from DSC.

The pure erythritol samples displayed an average crystallization temperature of 8.47 °C, a supercooling degree of 114 °C, and a thermal utilization efficiency of 34.0% (Table 2). In contrast, the average values for the **Ery/Ery-2F** = 99:1 mixing ratio sample were 59.7 °C for crystallization temperature, 61.6 °C for the degree of supercooling, and 74.4% for thermal utilization efficiency. The degree of supercooling was minimal, and the thermal utilization efficiency was higher for the mixed samples compared to any of the pure erythritol cycles, with similar standard deviations. These findings suggest that this specific mixture ratio maintains a stable supercooling suppression effect and may serve as a superior PCM compared to pure erythritol. Numerical data for cycle measurements are provided in the Supporting Information (Tables S1 and S2).

As evidenced from the results in Table S2, the ΔH value continually decreased following the repeated heating and cooling treatments. This likely stemmed from the vaporization or thermal decomposition of the **Ery-2F** additive to **Ery**, as discussed in Section 3.1.

3.3. Erythritol and 2,2,3,3-Tetrafluoro-1,4-butanediol.

In the preceding section, it was demonstrated that the use of fluorine-substituted analogues effectively suppresses supercooling in pure erythritol. However, the impact of the number of fluorine atoms within these analogues remains uncertain. This section conducts further investigation on analogues with an increased number of fluorine atoms (**Ery-4F**). Figure 4 presents the DSC data measured for three cycles for the **Ery** and **Ery-4F** mixture samples, with Table 3 detailing the thermal properties obtained from the DSC.

Figure 4a shows the DSC data for samples mixed with **Ery** and **Ery-4F** in ratios of 100:0, 75:25, 50:50, 25:75, and 0:100. Similar to the mixtures of **Ery** and **Ery-2F**, the melting points of the mixtures were lower than that of a pure substance based on the melting point depression. Regarding crystallization temperature, no peak was detected for **Ery-4F** after the first cycle's crystallization peak. Figure 4 shows that heat flow gradually decreased at temperatures higher than the melting point peak, suggesting heat release outside the system through the gap between the pan and the lid. Sample mass loss was confirmed by TG−DTA (Figure S4). As illustrated in Figure S4, **Ery-4F** exhibited an endothermic peak at approximately 80 °C, while sample weight loss manifested during heating to 140 °C. This behavior implied the potential vaporization or thermal decomposition of **Ery-4F** during the DSC measurements, suggesting that the sample composition of the **Ery** and **Ery-4F** mixture might undergo slight alterations during this process, similar to the phenomenon observed for **Ery-2F**.

Almost no clear crystallization peaks were detected in the mixture. Although high crystallization temperatures and enthalpies were observed in the first cycle of the **Ery**/**Ery-4F** = 75:25 mixing ratio, they could not be confirmed in subsequent cycles, indicating that neither the mixture nor pure **Ery-4F** addressed the supercooling problem. However, the mixing ratios of 99:1, 95:5, and 90:10 with mixtures of **Ery** and **Ery-2F** tended to suppress supercooling, so the same mixing ratios were also evaluated in mixtures of **Ery** and **Ery-4F** (Figure 4b). Compared with the results in Figure 4a, the crystallization peak was slightly clearer. However, none of the mixing ratios resulted in clear supercooling inhibition. These findings indicate that fluorine analogue **Ery-4F** does not crystallize, and mixing it with **Ery** has no effect on supercooling control. The thermal utilization efficiency of **Ery-4F** is almost the same as or lower than that of pure erythritol, suggesting no advantage to mixing **Ery-4F**. Multiple crystallization peaks were observed in some cases, similar to the mixture of **Ery** and **Ery-2F**, necessitating clarification of respective crystallization phases in future investigations.

A summarized graph of the two graphs shown in Figure 4 is shown in Supporting Information for easy comparison (Figure S5).

3.4. Relationship between Thermal Properties and Molecular Structure.

From the above experiments, the effect of supercooling suppression was observed for some ratios in the mixing of **Ery-2F**, whereas no effect of supercooling suppression was observed in the mixing of **Ery-4F**. One contributing factor could be the difference in the number of hydrogen bonds. While **Ery** possesses four hydroxyl groups capable of forming hydrogen bonds, the potential for hydrogen bond formation may differ in **Ery-2F** and **Ery-4F**. This disparity arises from the fact that oxygen atoms in hydroxyl groups have two noncovalent electron pairs available for hydrogen bonding, whereas the fluorine atoms under consideration have three such pairs. This difference in the number of hydrogen bonds formed is thought to cause a change in intermolecular interactions. Although it is currently unclear whether hydrogen bond formation between C−F···HO is possible,[24] the supercooling suppression in this experiment indicates that hydrogen bonding between C−F···HO may occur. Another factor could be the size of functional groups. As noted in the objective section, this study introduces fluorine, which is relatively close in size to the hydroxy group. Therefore, the molecular sizes of **Ery** and **Ery-2F** are considered to be similar. However, in **Ery-4F**, four fluorines are introduced at the 2- and 3-positions, which increases the molecular size compared to **Ery**. This suggests that when **Ery** and **Ery-4F** were combined, it was difficult for the molecules to mix with each other, and the intermolecular interactions did not differ. In contrast, when **Ery** and **Ery-2F** were combined, the molecules mixed well and the change in intermolecular interactions suppressed the supercooling.

In the future, it is necessary to further investigate the effects of substituents and crystal structures on suppressing supercooling of sugar alcohol compounds.

4. CONCLUSION

In summary, it was experimentally verified that mixing a small amount of 2,3-difluorobutane-1,4-diol (**Ery-2F**) with erythritol (**Ery**) is effective in suppressing supercooling and that supercooling can be suppressed by adjusting intermolecular hydrogen bonds (interactions). In particular, a mixing ratio of **Ery**/**Ery-2F** = 99:1 was found to suppress supercooling by 52.4 °C and retain a crystallization enthalpy higher than **Ery**, which is in practical use as a latent heat storage material. Cycle measurements also suggest that this mixed sample is stable and effective in suppressing supercooling.

This technique is easy to perform and use in practical applications, suggesting the possibility of using this material as an efficient latent heat storage material. In the future, the relationship. Future investigations will explore the correlation between supercooling suppression and crystal form.

In this study, a physical mixture of **Ery** and an additive (**Ery-2F** or **Ery-4F**) was used as is for DSC measurements. However, mass loss due to additive volatilization or thermal decomposition was observed. For samples of erythritol with additives added for DSC measurement, it is necessary to quantify the mass loss caused by evaporation and thermal decomposition of the additives during repeated heating and cooling. It is also thought that this mass loss can be reduced by encapsulating the sample in silica or similar material. These topics will be the subject of future research.

ASSOCIATED CONTENT

Data Availability Statement

The data supporting the findings of this study are available throughout the manuscript and Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c09309.

> Figure S1 Synthesis scheme of 2,3-difluorobutane-1,4-diol (**Ery-2F**). Figure S2 TG−DTA curve of **Ery-2F**. TG−DTA measurement were carried out under N2 flow (100 mL/min) between 30 and 130 °C. Both heating both heating and cooling rates were set at 5 °C/min, but the rate of descent was slower than 5 °C/min below about 100 °C due to natural cooling. Figure S3 DSC data in mixed samples of **Ery** and **Ery-2F**. (**Ery/Ery-2F** = 100:0, 99.5:0.5, 99:1, 95:5, 90:10, 75:25, 50:50, 25:75, 0:100 from top to bottom.) Table S1 Results of cycle measurement of pure erythritol (**Ery**). Table S2 Results of cycle measurement of the sample with a mixing ratio of 99:1 of **Ery**/**Ery-2F**. Figure S4 TG−DTA curve of **Ery-4F**. Measurement condition was same as Figure S2. Figure S5 DSC data in mixed samples of **Ery** and **Ery-4F**. (**Ery**/**Ery-4F** = 100:0, 99:1, 95:5, 90:10, 75:25, 50:50, 25:75, 0:100 from top to bottom) (PDF)

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Notes

The authors declare no competing financial interest.

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