Article

Surface Roughness-Governed Shape Stability of the Coal Fly Ash-Based Phase Change Material: Molten Salt Processing and Thermal Properties

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Abstract: Coal fly ash (FA) valorization is of great significance and sustainable interests to addressing the current environmental challenges faced by coal power industry. Herein, this work attempted a novel molten salt Na_2CO_3 treatment for processing FA into a robust matrix to support lauric acid (LA) toward construction of latent phase change composite. Their micromorphology, physiochemical, and thermal properties were monitored with scanning and transmission microscopy, X-ray diffraction and FT-IR spectroscopy, differential scanning calorimetry, among others. As Na_2CO_3 dosage increased from 20% to 40%, the FA experienced firstly higher loss of SiO_2 and then substantial loss of Al_2O_3 , and yet exhibited merely varied porosity. Then, both the composites revealed a maximum LA content of 20% that doubled that of pristine FA. Nevertheless, the optimal composite was disclosed with thermal conductivity of 0.5668 W/mK, which was 69% higher than its FA-based counterpart. It was proposed that the surface roughness evidenced by the formation of tremendous grooves and gaps during thermal alkaline processing were accountable for the promoted carrying capacity toward organic component. Furthermore, the latent phase change composite revealed excellent durability, including negligibly varied phase transition temperature and enthalpy even after 1500 thermal cycling, which promised great interest in passive building cooling. Meanwhile, the finds here led to a new understanding into the structural origin of adsorption capacity by inorganic FA, and may provide guidance for better exploration of its characteristics for other applications.

Keywords: fly ash; molten salts; surface roughness; enhanced thermal conductivity; phase change material

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1. Introduction

Coal accounts for over 85% of China's primary energy reserves, and coal power offers over 60% in total energy supply each year in China. Fly ash (FA), as a well-known byproduct of coal power plants that is mostly constituted of SiO_2 and Al_2O_3 , had therefore become one of the most produced solid wastes in bulk [1]. Conventional disposal including dumping or burial imposed great threat over surroundings and public health. Thus, to find a rational way of utilization at large scale is critically important to address the above issues. Given its inorganic nature, FA shows great promise for constructing materials [2,3]. Nevertheless, it was mainly used as structural or additive components. Exploration of FA-based materials with designed functionalities by full exploitation of its physiochemical feature is of continuous interest for valorization of this kind of solid waste.

The currently increasing worldwide concerns over global climate and environment changes has especially driven tremendous efforts into the improvement of energy conversion and utilization efficiencies. In particular, the building energy consumption was estimated to be as high as 33% of annual total social energy consumption in China. With decent energy storage density, customizable thermal properties, and flexible applicability, latent phase change material therefore received great interest for passive building energy conservation and solar energy storage systems, among others [4,5]. By virtue of the high latent heat, near ambient phase transition temperature, excellent thermal, volumetric, and chemical stability, and negligible vapor pressure, lauric acid (LA) was widely used as an active component for constructing various kinds of phase change materials [6–8]. Meanwhile, to guarantee the reversible transition in practical use, the active components were usually integrated into a solid matrix, so far, expanded graphite, aerogels made up of graphene and carbon nanotubes [9,10], kaolin clay, diatomite [6,11], expanded perlite [12,13], mesoporous silica [14], TiO_2 [15], etc., most of which possess considerable amount of diverse porosity and, to some extent, valuable products in many industries. The waste FA would be a competent candidate with regard to economic concerns, yet, its naturally poor carrying capacity strongly hindered the application as matrix for functional composites design. On the other hand, most of the previous work emphasizes the importance of matrix porosity, either naturally-occurring or post-created, in the latent phase change composite; while little attention has been given to potential of surface roughness, not mentioning its contribution to final thermal properties and stability [16,17].

In this work, a novel molten salt Na_2CO_3 treatment was attempted for processing FA into a robust matrix to support lauric acid (LA) toward construction of latent phase change composite. The micromorphology, physiochemical, and thermal properties of a series of resultants was monitored with scanning and transmission microscopy, X-ray diffraction and FT-IR spectroscopy, differential scanning calorimetry, among others. Interestingly, it was revealed that the surface roughness instead of porosity was responsible for the enhancement of adsorption capacity of modified FA (mFA), which enabled both the phase change enthalpy and excellent thermal durability. Along with the dramatically promoted thermal conductivity, the hybrid materials are promising for passive energy saving in building structures. Moreover, the finding here provided a further understanding of the carrying capacity of inorganic fly ash.

2. Experimental

2.1. Materials and Chemical Reagents

Commercial fly ash was purchased from Gongyi Filter Material Limited Company (Gongyi City, China). Lauric acid (LA) and sodium carbonate, both of analytical grade, were purchased from Shanghai Dibo biotechnology Limited Company (Shanghai City, China) and Tianjin Qilun Chemical Science and Technology Limited Company (Tianjin, China), respectively.

2.2. Thermal Molten Salt Processing of Fly Ash

The fly ash was modified by facile thermal processing with Na_2CO_3 . The weight ratio of Na_2CO_3 to fly ash was from 0.2 to 0.4. After adding Na_2CO_3 , the mixture was loaded into a ceramic boat and subjected to 900 °C treatment. When naturally cooled to room temperature, the mixture was washed with distilled water, and the thermal alkaline-modified fly ash (mFA) was obtained after desiccation at 80 °C.

2.3. Preparation of Phase-Change Composite Material (PCCM)

The preparation of phase-change composite material (PCCM) followed a vacuum-assisted impregnation method, as shown in Figure 1. Typically, the mixture of LA and FA with set ratio was fully mixed before being transferred into the vacuum drying oven, which was further vacuumed and elevated to 80 °C for 1 h. After then, the pressure was recovered. This operation was repeated three times to facilitate the adsorption of LA into FA matrix.

Finally, the fresh PCCM was kept under the vacuum and 80 °C overnight before being naturally cooled to ambient temperature. The optimal ratio was determined by diffusion test. Namely, the composite was pressed into a column with height of 0.2 cm and diameter of 1.3 cm, and then placed on top of a filter paper at 60 °C for 1 h. Thus, the leakage of LA can be visually observed by the color change from the paper. Finally, the optimum loading amount for FA, 0.2 mFA, and 0.4 mFA were 10%, 20%, and 20%, respectively.

Figure 1. Block diagram of synthesis procedure.

2.4. Characterizations

The micromorphology was obtained with scanning electron microscopy (SEM, Hitachi S-4800, Japan). X-ray fluorescence (XRF) analysis was performed with analyzer from AxiosmAX Petro, Netherlands. Differential scanning calorimetry (DSC) profiles were recorded with low-temperature analyzer (HDS CPT500LT/1400, German). The N_2 isothermal adsorption-desorption profiles were studied with the automated gas sorption analyzer (SI-MP-10, Quadrasorb, Quantachrome, USA) at 77 K, while the specific surface area was obtained basing on the Brunauer–Emmett–Teller method. The thermal conductivity was tested by a TPS2500S/TPS2500S analyzer (Hot Disk, Sweden), and the corresponding test range was 0.005–1800 W/(mK). FT-IR spectra were acquired with FTIR TENSOR27 spectrometer.

3. Results and Discussion

Figure 2 depicts the brief preparative procedures of PCCMs. The pristine FA was fully mixed with a certain amount of Na_2CO_3 and subjected to heating treatment. After being cooled down, the resultant was washed with distilled water, and the mFA with reconstructed surface was obtained. After vacuum adsorption above molten point of LA, the PCCMs named LA/ x mFA were then acquired, where x is the weight ratio of Na_2CO_3 to FA.

Figure 2. Schematic illustration of the composite preparation.

Figure 3 revealed the micromorphology of FA, 0.2 mFA, 0.4 mFA, and their LA-loaded counterparts. In Figure 3a, the pristine FA was generally demonstrated as particulate-decorated microspheres, yet, the surface exposed around those particulates was quite smooth. After LA loading, many tiny particles emerged, accompanied by the appearance of irregular mass in between different microspheres (Figure 3b). Despite Na_2CO_3 processing at high temperature, the resultant 0.2 mFA and 0.4 mFA maintained their spherical body. Yet, both revealed significantly enhanced surface roughness. Furthermore, many chips-like structures were observed around the surface of 0.2 mFA, as shown in Figure 3c, this can be ascribed to the strong etching effect by Na_2CO_3 . By contrast, the LA/0.2 mFA had a relatively smoother surface. It is proposed that the vacuum loading process above melting point of LA could facilitate the organic fluid being well absorbed into the gaps under the chips, also filled into the grooves over the sphere. Finally, the surface seemed “repaired”. In the case of 0.4 mFA, a similar situation was observed. The spheres in Figure 3f were wrapped with syncretic LA flakes.

The component variation during molten Na_2CO_3 treatment was monitored by XRF analysis. As shown in Table 1, the pristine FA had SiO_2 content of 55.67%, nearly double that of Al_2O_3 . Na_2CO_3 is reactive to both the SiO_2 and Al_2O_3 . Therefore, with lower Na_2CO_3 dosage, more of the alkaline tended to react with SiO_2 due to the higher content-offered contact opportunity. Thus, the relative proportion of Al_2O_3 to SiO_2 actually increased from 0.5 to 0.54. When higher Na_2CO_3 dosage was applied, this ratio dropped to 0.46 in the case of 0.4 mFA. Moreover, the XRD patterns of FA, 0.2 mFA, 0.4 mFA, LA/0.2 mFA, LA/0.4 mFA, and LA are provided in Figure 4. The noticeable peaks around 17.1° , 22.4° , 27.5° , and 33.8° are attributable to characteristic signals of the mullite phase [18–22]. Meanwhile, the SiO_2 was supposed to be primarily amorphous since no noticeable peak was revealed for quartz. By indexing with XRD standard card, the newly appeared peaks at 20.5° , 21.3° , 23.2° , 27.3° , and 29.4° can be ascribed to the diffractions by 020, 002, 201, 210, and 202 plane in NaAlSiO_4 [23–27]. The pure LA displayed two distinct peaks at 22° and 24.5° [18,28–31]. Furthermore, the composite showed integrated diffraction patterns of modified fly ash and LA without newly appeared signals, suggesting the physical interactions were accountable for their combination. In addition, the LA dispersed in both 0.2 mFA and 0.4 mFA remained crystalline, this provided the basis for latent energy storage. To reveal the effect of molten salt processing on the porosity, nitrogen isothermal adsorption and desorption analysis was then performed, and the corresponding profiles of FA, 0.2 mFA, and 0.4 mFA were plotted in Figure 5a. The three samples revealed generally the same adsorption and desorption behavior, and the specific surface area were found to be 0.7, 0.6, and $0.5 \text{ m}^2/\text{g}$, respectively, suggesting negligible changes. Meanwhile, the pore diameter are mostly below 40 nm.

Figure 3. SEM images of: (a) fly ash (FA); (b) lauric acid (LA)/FA; (c) 0.2 modified fly ash (mFA0); (d) LA/0.2 mFA; (e) 0.4 mFA and (f) LA/0.4 mFA.

Table 1. Components of FA and mFA by X-ray fluorescence (XRF) analysis.

Compound	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	Na ₂ O	Others
FA	55.67	27.91	5.36	5.03	0.4	5.63
0.2 mFA	47.20	25.61	6.02	5.68	10.22	15.49
0.4 mFA	47.84	21.81	4.67	5.27	15.82	20.41

Figure 4. XRD patterns of FA, 0.2 mFA, 0.4 mFA, LA/0.2 mFA, and LA/0.4 mFA.

Figure 5. (a) Nitrogen isothermal adsorption and desorption profiles and (b) pore size distribution.

The chemical structures of bare FA and LA and the composites were characterized with FT-IR across a range of 500–4000 cm^{−1}. As shown in Figure 6, the wide adsorption at 1102 cm^{−1} was ascribed to the characteristic stretching vibration of the Si-O bond [32–36]. This peak can be easily identified within the curves of both 0.2 mFA and 0.4 mFA. The pure LA showed multiple characteristic absorptions across in the range from 3000 to 1500 cm^{−1} [31,37–40]. Two of them located at 2918 and 2850 cm^{−1} were due to the stretching vibrations of -CH₂ and CH₃, whilst the one at 1695 cm^{−1} was attributable to the adsorption by carboxylic groups at the end of each molecule chain. All these featured peaks appeared in those composites, which suggested the successful loading of LA in the matrix. Furthermore, no new peak was found, therefore, the hybrid had formed in a physical manner, which is consistent with the result from above XRD analysis.

Figure 6. FT-IR spectra of FA, 0.2 mFA, 0.4 mFA, LA/0.2 mFA, LA/0.4 mFA, and LA.

Thermal conductivity is one of the most important factors for phase change composites. Herein, the thermal conductivity was then measured by a transient plane source method, where the samples were required to be shaped into cylinder. However, the attempt with FA failed due to the intrinsically poor interactions between those inorganic particulates. By contrast, the LA introduced into FA functioned as an adhesive and rendered the composite with benign moldability, and the thermal conductivity was then determined to be 0.3344 W/mK. Interestingly, even with higher loading of LA, both phase change composite with modified FA revealed significantly enhanced thermal conductivity. The value of LA/0.2 mFA and LA/0.4 mFA were 0.5668 W/mK and 0.5141, which are 69% and 54% higher than that of the LA/FA. Given the structural transition revealed above, it was proposed that the relatively higher amount of residual Al₂O₃ in the matrix at lower dosage

of molten Na_2CO_3 would provide more rapid thermal diffusion pathways. The higher loss of Al_2O_3 in LA/0.4 mFA therefore led to slightly decreased thermal conductivity, yet still higher than its unmodified counterpart.

DSC was further applied to disclose the texturally thermal storage capacity of LA and three phase change composites. Figure 7 showed their DSC profiles. All displayed obvious supercooling phenomenon. The melting and freezing points and corresponding phase change enthalpy (ΔH_m) was summarized in Table 2. To be specific, the T_m and T_c for pure LA, LA/FA, LA/0.2 mFA, and LA/0.4 mFA were 43.1 and 40.3 °C, 42.3 and 38.5 °C, 39.5 and 32.1 °C, and 39.7 and 32.4 °C. Meanwhile, the freezing point showed evident decrease. As the solidification of LA followed typical crystallization manner, the rigid surface of FA may provide tremendous heterogeneous nucleus sites, which thus initiate the rearrangement of flexible LA molecule chains at lower temperature. After etching by molten salts, the surface became significantly rougher, thus the freezing point further decreased with LA/0.2 mFA and LA/0.4 mFA. Meanwhile, the reverse melting behavior also tended to occur at lower temperature. On top of that, the reinforced thermal conductive performance by inorganic structures may also facilitate the heat transfer in the composites. Finally, the phase change temperature window was well fitted with ambient temperature (30–45 °C). Therefore, such hybrid composite may function as active component for heat storage in passive energy-saving building structures, which help to reduce the indoor temperature amplitude.

Figure 7. Differential scanning calorimetry (DSC) curves of LA, LA/FA, LA/0.2 mFA, and LA/0.4 mFA.

Table 2. Phase transition temperature and corresponding enthalpy.

PCM	Heating Process		Cooling Process	
	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
LA	43.1	186.6	40.3	183.5
LA/FA	42.3	16.7	38.5	15.8
LA/0.2 mFA	39.5	34.1	32.1	31.3
LA/0.4 mFA	39.7	31.5	32.4	27.6

In the DSC process, the integration of endothermic and exothermic peak area generally tells phase change enthalpy. As listed in Table 2, the ΔH_m and ΔH_c for LA, LA/FA, LA/0.2 mFA, and LA/0.4 mFA were 186.6 and 183.5 J/g, 16.7 and 15.8 J/g, 34.1 and 31.3 J/g, and 31.5 and 27.6 J/g, respectively. Basically, phase change enthalpy was supposed to be proportional to the content of the organic part within the phase change composites, then,

the theoretical ΔH_m and ΔH_c of phase change for the above three were calculated to be 18.7 and 18.4 J/g for LA/mFA, and 37.32 and 36.7 J/g for the other two. The slightly lower ΔH in both melting and freezing processes can be explained as follows: due to the confining effect by solid matrix, part of the LA molecules could be trapped at the coarse surface, which lose the ability to participate the bulky melting and crystallization. Therefore, there is no contribution of the overall latent heat storage or release.

Regarding practical application, the thermal durability would become greatly important. Then, all three composites were subjected to 1000 thermal cycling to see if the phase change temperature or enthalpy would change. Figure 8a,b provided the DSC profiles before and after thermal cycling test, respectively. The supercooling phenomenon still existed. Moreover, the textural thermal factors were given in Table 3. The T_m and T_c of LA/FA merely remained unchanged, however, the ΔH_m and ΔH_c was substantially dropped. More than a half was lost. This can be attributed to the weak adsorption capacity of FA toward organic LA, which arose from its relatively smooth surface. On the contrary, the T_m and T_c of LA/0.2 mFA and LA/0.4 mFA slightly increased, yet was still below 45 °C. More importantly, the ΔH_m and ΔH_c only showed maximum loss by 9.3% even after 1500 cycles, suggesting the excellent thermal stability. The rough surface created by molten salts etching should account for such excellent durability.

Figure 8. DSC curves of LA, LA/FA, LA/0.2 mFA, and LA/0.4 mFA: (a) before 1500 thermal cycles; (b) after 1500 thermal cycles.

Table 3. Textural thermal properties of LA/FA, LA/0.2 mFA and LA/0.4 mFA before and after 1500 thermal cycles.

PCM	Cycles	Heating Process		Cooling Process	
		T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
LA/FA	0	42.3	16.7	38.5	15.8
	1500	41.9	7.5	38.9	6.5
LA/0.2 mFA	0	39.5	34.1	32.1	31.3
	1500	40.8	32.3	37.6	28.4
LA/0.4 mFA	0	39.7	31.5	32.4	27.6
	1500	42.2	30.9	38.9	26.7

4. Conclusions

In summary, we proposed the thermal treatment of FA with molten salt Na_2CO_3 to introduce significant surface roughness. When used as solid matrix for LA loading, the resultant exhibited doubled loading capacity of 20%, which can be ascribed to strong adsorption effect by those surface grooves and gaps. Furthermore, the present phase change composites exhibited significantly enhanced thermal conductivity up to 0.5668 W/mK, due to the increased proportion of Al_2O_3 by etching effect. Meanwhile, the melting and crystallizing remained around that of pure LA and well located within the range from 30 °C to 45 °C. In addition to excellent working durability even after the 1500 thermal

cycling test, the composite offered great promise for application in passive energy-saving building structures. The finding here may provide new insights for design guidance toward FA-based functional composites.

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