Thermal performance enhancement of erythritol/carbon foam composites via surface modification of carbon foam

Junfeng Li*, Wu Lu, Zhengping Luo and Yibing Zeng

Aerospace Research Institute of Materials and Processing Technology, Beijing 100076, China

E-mail: *jfli1227@126.com

Abstract. The thermal performance of the erythritol/carbon foam composites, including thermal diffusivity, thermal capacity, thermal conductivity and latent heat, were investigated via surface modification of carbon foam using hydrogen peroxide as oxider. It was found that the surface modification enhanced the wetting ability of carbon foam surface to the liquid erythritol of the carbon foam surface and promoted the increase of erythritol content in the erythritol/carbon foam composites. The dense interfaces were formed between erythritol and carbon foam, which is due to that the formation of oxygen functional groups C=O and C-OH on the carbon surface increased the surface polarity and reduced the interface resistance of carbon foam surface to the liquid erythritol. The latent heat of the erythritol/carbon foam composites increased from 202.0 to 217.2 J/g through surface modification of carbon foam. The thermal conductivity of the erythritol/carbon foam composite before and after surface modification further increased from 40.35 to 51.05 W/(m·K). The supercooling degree of erythritol also had a large decrease from 97 to 54 ℃. Additionally, the simple and effective surface modification method of carbon foam provided an extendable way to enhance the thermal performances of the composites composed of carbon foams and PCMs.

Keywords: erythritol, carbon foam, surface modification, thermal conductivity, supercooling degree

1. Introduction

Phase change materials (PCMs) for thermal energy storage and thermal management have attracted a great deal of attention due to its high thermal energy storage density and small temperature variation. A lot of inorganic and organic PCMs, including paraffin, fatty acids, hydrated inorganic salts, and polyols, have been widely applied in many fields, such as the thermal control of the electronic devices, industrial waste heat recovering, and solar energy utilization [1-6]. Among these various kinds of PCMs, erythritol ($C_4H_{10}O_4$), containing four hydroxyl groups, has high latent heat of 347.7 kJ/kg, is not poisonous and corrosive, and is low volatile. However, erythritol has the same problem as ther other organic PCMs, that is, low thermal conductivity, which decrease the heat transfer rate between a heat sourse and PCMs.

To increase the thermal conductivity of PCMs, Many kinds of high thermal conductivity materials, including metal foams [7-10], fins [11,12], graphite [13-19], carbon fibers [20-24], carbon foam [25-27], are used to form composites with PCMs and increase the heat transfer from a heat sourse to PCMs. Among these high thermal conductivity materials, carbon foam has low bulk density and good chemical inertness as well as high thermal conductivity, which are beneficial to derease the weight of

thermal energy storage system or thermal management system, and increase the systems' operational stablity. Many studies using carbon foam as thermal performance enhancer have been done.

Guo et al. [28] used graphite foams to enhance the thermal diffusivity of paraffin. They found that the structure of graphite foam, such as pore sizes, ligament thickness, has important effects on the thermal diffusivity and the thermal capacity, and large pore size and thinner ligament in graphite foam resultes in a larger latent heat but a lower thermal diffusivity. Lafdi et al. [29] prepared the composites composed of paraffin wax and carbon foam matrices with different porosities and thermal properties, and experimentally and numerically investigated the thermal characteristics of the composites. They found that the carbon foam matrix with higher porosity has more stability of thermal performance. Fleischer et al. [27] studied the influences of graphite foam, aluminium foam, and graphite nanofibers on the thermal performance and energy storage capabilities of paraffin wax. The study shows that the graphite foam is a more effective thermal conductivity enhancer for the infiltrated paraffin, and the paraffin melts rapidly, without exhibiting any significant delay to steady-state.

Carbon foam generally has high prosity, more than 70%, and hence has a high interface/volume ratio. Surface driven properties such as surface polarity and bond formation with the stuffing materials are crucial for applicability. However, few work focus on how the chemical affinity of interfaces between carbon foam and PCMs affects the thermal performance of composites. Thus this study is designed to study the thermophysical properties of the erythritol/carbon foam composites before and after the controlled surface modification of carbon foam.

In the present work, the effects of controlled surface modification of carbon foam on the thermal performance of the erythritol/carbon foam composites, including latent heat, thermal conductivity, thermal diffusivity, thermal capacity, and supercooling degree, are investigated. The microstructural changes of carbon foam surface before and after surface modification are also studied by a Fourier-transform infrared (FTIR) spectrometer and an optical microscope.

2. Experimental

The carbon foams were cut into small bulks (30mm×30mm×15mm), and part of them were suface-modified in the hydrogen peroxide at 90 ℃ for 2 h, respectively. The solid erythritol was completely melted at 150℃ in an oven. Then the suface-modified and starting carbon foam bulks were immersed into the liquid erythritol under vaccum for about 20 min until the liquid erythritol solidified. The above immersing process was repeated for three times, which ensured the pores of carbon foam can be adequately filled with the liquid erythritol.

The weight of carbon foam and the erythritol/carbon foam composites were recorded and used to calculate the weight and volume of erythritol filled in per gram of carbon foam. According to the latent heat of pure erythritol, the unit latent heat of the composites was caltulated. Meanwhile, the unit latent heat of the composites was also measured by a differential scanning calometer (DSC, 204F1, Netzsch, Germany) with a heating speed of 5 ℃/min. Optical microscopy images were obtained using an optical microscope (DM2500P, Leica, Germany). The FTIR spectroscopy of carbon foam before and after surface modification were obtained by a Fourier-transform infrared spectrometer (FTS3000, BIO-RAD, USA) with a resolution of 4 cm^{-1}. The thermal parameters were measured at room temperature using the laser flash technique (LFA427, Netzsch, Germany), and the sample sizes were Φ12.6 mm×1.5 mm.

3. Results and discussion

Figure 1 shows the photos and optical microscopy images of carbon foam and erythritol/carbon foam composites. The photos of carbon foam and erythritol/carbon foam composites are given in figure 1(a), (b), and (c), and their optical microscopy images are given in figure 1(d), (e), and (f) respectively. The images show that the pores in surface-modified carbon foam are completely filled with the erythritol (figure 1(f)), while there are lots of pores just partly filled with the erythritol in the no surface-modified carbon foam (figure 1(e)). This result indicates that surface modification of carbon foam has effectively increased the wetting ability of liquid erythritol to the carbon foam surface. Moreover, the

liquid erythritol is much easier to get into the carbon foam pores, and hence the dense erythritol/carbon composite is formed.
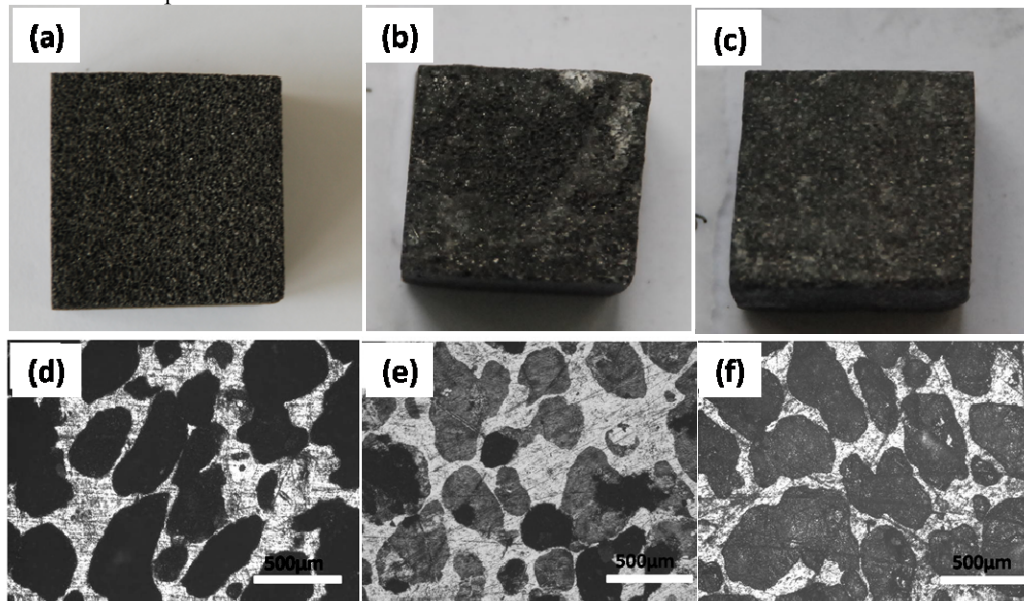
Figure 1. Photos and OM images of (a) photos of starting carbon foam (b) the composite of starting carbon foam and erythritol and (c) the composite of surface-modified carbon foam and erythritol. (d), (e), and (f) are the corresponding microstructures of the samples (a), (b), and (c), respectively.
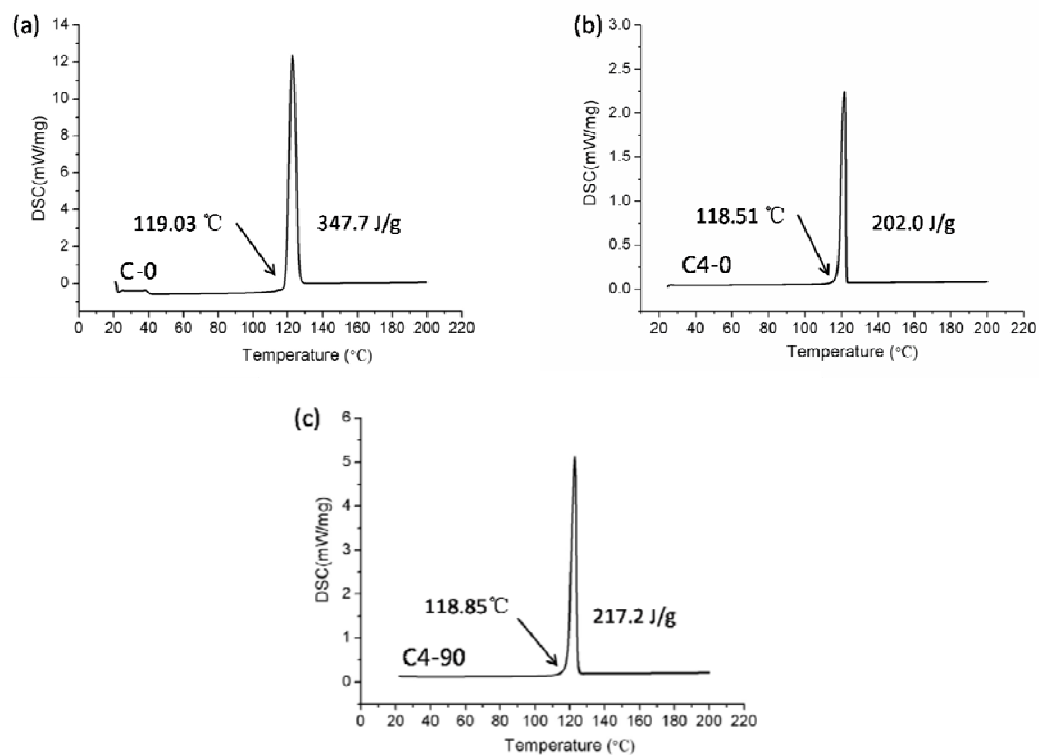
Figure 2. DSC curves of (a) erythritol, (b) starting carbon foam/erythritol composites and (c) surface-modified carbon foam/erythritol composites.

Figure 2 shows the influences of surface modification of carbon foam on the latent heat of the erythritol/carbon foam composites. It is found that the carbon foam has almost no effect on the shape

of endothermal peaks and the melting point of erythritol, 119.03 ℃ for pure erythritol, 118.51 ℃ for the sample C4-0, and 118.85 ℃ for the sample C4-90. The latent heat of the samples C-0, C4-0, and C4-90 was 347.7, 202.0, and 217.2 J/g measured by DSC, respectively. For the sample C4-90, there is a increase of 15.2 J/g, increasing by 7.5% compared with that of the sample C4-0. This latent heat increase is accorded with the microstructure changes in figure 1, that is, there is more erythritol in the carbon foam pores after the surface modification of carbon foam

Table 1 shows the thermal diffusivity, thermal capacity, and thermal conductivity of starting carbon foam and erythritol/carbon foam composites. The thermal diffusivity of the erythritol/carbon foam composites increases from 19.749 to 23.892 mm^2/s before and after the surface modification of carbon foam, increasing 20.98%. The thermal capacity of the erythritol/carbon foam composites also increases from 1.287 to 1.346 J/(g·K) with the density increasing. The thermal conductivity correspondingly increases from 40.35 to 53.06 W/(m·K), increasing 31.50% in the condition of no changes in the porosity and pore structure of carbon foam. The pure erythritol has a large supercooling degree of 97℃, while the supercooling degree of the samples C4-0 and C4-90 dramatically decreases to 56℃ and 54℃, respectively. The result indicates that the carbon foam can promote the crystallization of erythritol in the freezing process and moreover reduce the supercooling degree of erythritol, and the surface modification of carbon foam can further reduce the supercooling degree of Erythritol.

Table 1. Thermal diffusivity, thermal capacity, and thermal conductivity of starting carbon foam and erythritol/carbon foam composites

| Sample	Thermal diffusivity (mm^2/s)	Thermal capacity (J/g·K^{-1})	Thermal conductivity (W/m·K)	Density (g/cm^3)	Supercooling degree (℃)
C-0	79.565	0.748	29.76	0.50	/
C4-0	19.749	1.287	40.35	1.58	56
C4-90	23.892	1.346	53.06	1.65	54

Note: The carbon foam of the sample C-0 is not surface-modified starting carbon foam. The carbon foam of the sample C4-0 is not surface-modified, and the carbon foam of the sample C4-90 is surface-modified at 90 ℃.

Figure 3 depicts FT-IR spectra of surface-unmodified carbon foam and surface modified carbon foam. The peaks at 1738, 1640, 1461, and 1388 cm^{-1} are attributed to the stretching or bending vibration of C=O, C-C, C-H, C-OH, respectively [30-32]. The peaks (1026~1104 cm^{-1}) corresponding to oxygen functional groups markedly increase after the carbon foam surface is oxided in hydrogen peroxide at 90 ℃. The formation of oxygen functional groups C=O and C-OH on the carbon surface increases the surface polarity. The erythritol contains four C-OH groups, and hence the liquid erythritol is also polar liquid. Therefore, the wetting ability of the liquid erythritol to the oxided carbon foam surface increases, which reduces the interface resistance of carbon foam surface to the liquid erythritol. Finally, the pores of the surface-modified carbon foam are completely filled with the erythritol.

The thermal performance enhancement of erythritol/carbon foam composites are also attributed to the dense interface formation between the erythritol and carbon foam, as shown in figure 4. It is found that the dense interfaces form not only in the flat interface but also in the curve interface. The dense interfaces are beneficial to reduce the interface thermal resistance and enhance the thermophysical properties of the composites.
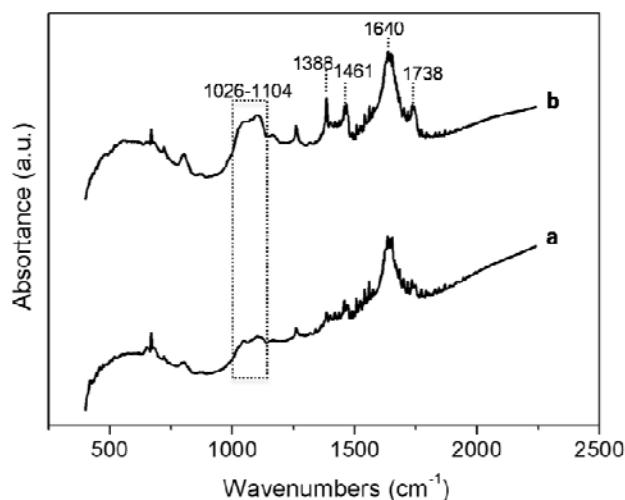
Figure 3. FT-IR spectra of (a) starting carbon foam and (b) surface-modified carbon foam.
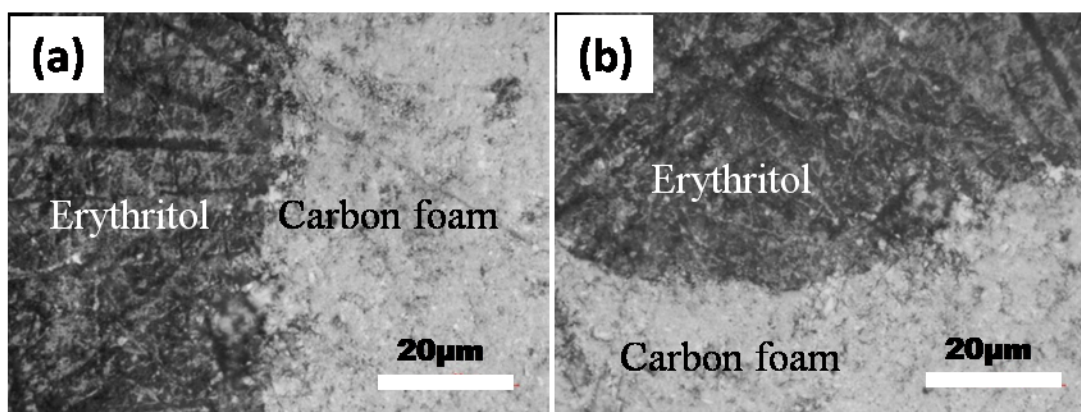
Figure 4. Interfaces between surface-modified carbon foam and erythritol in the sample C4-90, (a) flat interface, (b) curve interface.

4. Conclusions

The thermal performance enhancements of erythritol/carbon foam composites in which carbon foam surface is modified using hydrogen peroxide as oxidizer have been demonstrated. There are carbonyl and hydroxyl groups formed on the carbon foam surfaces after the surface modification, and the polarity of carbon foam surface increases, which enhances the wetting ability of polar liquid erythritol to the carbon foam surface. The pores of surface-modified carbon foam are completely filled with the erythritol, and the dense interfaces form between the carbon foam surface and erythritol. Moreover, the thermal diffusivity, thermal capacity, thermal conductivity, and latent heat of the erythritol/carbon foam composites are markedly improved. There is an increase of 15.2 J/g for the sample C4-90, increasing by 7.5% compared with that of the sample C4-0. The thermal conductivity of the erythritol/carbon foam composite before and after surface modification further increases from 40.35 to 53.06W/(m·K). The supercooling degree of erythritol has a large decrease from 97 to 54 ℃. In addition, the carbon foam, whose surfaces are modified by this simple and effective method, is also able to form dense composites with other polar PCMs. The surface modification of carbon foam provides an extendable route for enhancing the thermal performance of the composites composed of carbon foams and PCMs.

Acknowledgements

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