PERGAMON

Energy Conversion & Management 41 (2000) 129–134

ENERGY CONVERSION & MANAGEMENT

www.elsevier.com/locate/enconman

Heat storage performance of the binary systems neopentyl glycol/pentaerythritol and neopentyl glycol/trihydroxy methyl-aminomethane as solid–solid phase change materials

Xiaowu Wang[a], Enrong Lu[b], Wenxian Lin[b,*], Tao Liu[b], Zhaoshun Shi[b], Runsheng Tang[b], Caizhang Wang[c]

[a]*Department of Applied Physics, South China University of Technology, Guangzhou 510642, People's Republic of China*

[b]*Solar Energy Research Institute, Yunnan Normal University, Kunming 650092, People's Republic of China*

[c]*Department of Physics, Yunnan Normal University, Kunming 650092, People's Republic of China*

Received 3 November 1998; accepted 16 May 1999

Abstract

In this work, an experimental study was conducted to investigate the heat storage performance of solid–solid phase change materials including the binary systems of NPG/PE and NPG/TAM, consisting of NPG (neopentyl glycol, $C_5H_{12}O_2$, PE (pentaerythritol, $C_5H_{12}O_4$) and TAM (trihydroxy methyl-aminomethane, $C_4H_{11}O_3N$).

Keywords: Solid–solid phase change material; Heat storage performance; Binary system; NPG ($C_5H_{12}O_2$); PE ($C_5H_{12}O_4$); TAM ($C_4H_{11}O_3N$)

1. Introduction

Compared to sensible heat storage, phase change heat storage has the advantages of bigger energy storage density, smaller volume, higher efficiency, fixed temperatures for charging and discharging, etc. At present, solid–liquid PCMs (phase change materials) are popularly studied

* Corresponding author. Department of Mechanical and Mechatronic Engineering, The University of Sydney, NSW 2006, Australia. Tel.: +61-2-9351-2591; fax: +61-2-9351-7060.

E-mail address: lin@orr.mech.eng.usyd.edu.au (W. Lin)

0196-8904/00/$ - see front matter
PII: S0196-8904(99)00097-7

and used but most of the solid–solid PCMs are not given enough attention due to their smaller latent heat and higher phase change temperatures which are undesirable in low temperature heat storage applications.

Solid–solid PCMs, when compared to solid–liquid PCMs, have the advantages of a smaller volume change during the phase change process, no leakage, smaller erosion to the device, longer lifespan, etc., though they do have the drawbacks of smaller latent heat and higher phase change temperatures. They are receiving more and more attention recently.

It is found that materials such as polyalcohols, polyethylenes and layered perovskites are the most promising solid–solid PCMs. Among the polyalcohols, NPG (neopentyl glycol, $C_5H_{12}O_2$), PE (pentaerythritol, $C_5H_{12}O_4$), TAM (trihydroxy methyl-aminomethane, $C_4H_{11}O_3N$) etc. are the highlights of researches [1–10]. At low temperature, these polyalcohols are heterogeneous, but they become homogeneous face-centred cubic crystals that have high symmetry and absorb a great deal of hydrogen bond energy when the temperature rises to their own solid–solid phase change temperatures. Experiments show that the polyalcohols experience a first-order phase transition during which the change in their Gibbs energy is zero [11].

To obtain solid–solid PCMs with a larger range of phase change temperatures, which is essential for low temperature heat storage applications, we can mix two or more polyalcohols with a fixed molecule ratio to form a kind of alloy mixture whose temperature can be adjusted according to the requirements of practical applications [12]. Some good work has been done on it [1–10]. Benson et al. [3], Zhang et al. [7] and Ruan et al. [1] employed DSC thermal analysis to study experimentally the solid–solid phase change temperature and enthalpy of the mixture of NPG and PE and found that there are two solid–solid phase transition peaks in the mixture, and their corresponding phase change temperatures and enthalpies are, respectively, smaller than those of pure NPG and pure PE.

In this work, an experimental study was conducted to investigate the heat storage performance of the binary systems of NPG/PE and NPG/TAM as solid–solid phase change materials.

2. Experiment details

NPG ($C_5H_{12}O_2$), PE ($C_5H_{12}O_4$) and TAM ($C_4H_{11}O_3N$) (Shanghai No.1 Chemical Reagent Works, China) are the materials used in the experiments. The experiments were conducted in a Shimadzu DT40 Thermal Analysis Instrument (Shimadzu, Japan). The main technical qualifications of the instrument and the experimental conditions in this work are: precision — 0.1°C, surrounding atmosphere-static nitrogen for DTG and 20 ml/min of flowing nitrogen for DSC, reference material — α-Al_2O_3, the rate to increase temperature is 5°C/min and the rates to decrease temperature are, respectively, 1°C/min (below 30°C), 0.5°C/min (below 20°C), and 0.2°C/min (below 10°C).

Preparation of experimental samples: put the mixture of NPG and PE or NPG and TAM which have been accurately weighed in accordance with the desired ratio into a mortar, pour pure ethyl alcohol into the mixture, illuminate it by an infrared light until the ethyl alcohol

totally volatilises, then take away the infrared light and cool the material to room temperature and finally, grind the material into powder.

Storage and sealing of experimental samples: put the well ground NPG/PE mixture into an aluminium container with the diameter of 5 mm and then add 2% (weight) graphite into it. Finally, put a small sheet of aluminium plate on the top of the container and crush it until it seals the container well. As for the mixture of NPG/TAM, the method of storage and sealing is similar to that of NPG/PE with the only difference being that a little silicone oil is dropped into the mixture of NPG/TAM (until the oil drenches the material).

3. Results and discussion

The experimental results of the heat storage performance of the binary systems of NPG/PE and NPG/TAM, under different molecule fractions, during the heating and cooling processes are given in Tables 1–4.

The experimental results can be summarised as follows:

1. There are two phase change peaks in the binary systems of the polyalcohols. The first phase change temperature is lower than that of the component which has the smaller molecule fraction in the mixture, and the second phase change temperature is also lower than that of the other component. The sum of the phase change enthalpies of the two peaks is lower

Table 1
Heat storage performance of the binary system of NPG/PE during the heating process

Fraction of NPG molecules	0.382	0.528	0.618	0.764	0.854	0.910
First solid–solid phase change temperature (°C)	32.0	34.0	35.2	37.0	37.4	36.6
Second solid–solid phase change temperature (°C)	169.8	160.3				
First solid–solid phase change enthalpy (J/g)	18.79	26.20	33.16	46.14	51.50	68.15
Second solid–solid phase change enthalpy (J/g)	147.73	83.02				
Instrument stopping temperature (°C)	21.4	22.9	19.8	27.4	21.6	12.8
Weight loss until instrument stops (%)	0.00	0.00	0.00	0.00	0.00	0.923

Table 2
Heat storage performance of the binary system of NPG/PE during the cooling process

Fraction of NPG molecules	0.382	0.528	0.618	0.764	0.854	0.910
First solid–solid phase change temperature (°C)	25.9	28.0	29.4	31.3	31.0	31.1
Second solid–solid phase change temperature (°C)	172.3	169.5				
First solid–solid phase change enthalpy (J/g)	18.76	26.14	33.14	35.83	51.74	67.45
Second solid–solid phase change enthalpy (J/g)	125.31	81.39				
Maximum temperature of experiments (°C)	205.6	205.6	70.4	65.0	70.6	65.8

Table 3
Heat storage performance of the binary system of NPG/TAM during the heating process

Fraction of NPG molecules	0.382	0.528	0.618	0.764	0.854	0.910
First solid–solid phase change temperature (°C)	35.6	36.1	36.6	37.7	38.1	38.6
First solid–solid phase change enthalpy (J/g)	27.08	43.64	62.19	75.29	121.03	143.30
Instrument stopping temperature (°C)	13.6	15.4	22.4	19.1	19.9	25.1
Weight loss until instrument stops (%)	0.00	0.00	0.00	0.00	0.00	0.00

Table 4
Heat storage performance of the binary system of NPG/TAM during the cooling process

Fraction of NPG molecules	0.382	0.528	0.618	0.764	0.854	0.910
First solid–solid phase change temperature (°C)	22.1	24.1	26.4	28.3	29.2	30.0
First solid–solid phase change enthalpy (J/g)	33.03	48.83	62.20	80.46	137.97	150.11
Maximum temperature of experiments (°C)	115.6	116.6	81.9	63.6	63.3	62.7

than the sum of the phase change enthalpies of the two components. The decrease between the second phase change enthalpy of the binary system NPG/PE with the smaller fraction of NPG and the phase change enthalpy of PE is larger than that between the first phase change enthalpy of NPG/PE with the larger fraction of NPG and the phase change enthalpy of NPG. The first phase change enthalpy of NPG/TAM is larger than that of NPG/PE having the same fraction of NPG in the system. Even when the fraction of NPG is over 0.854, the phase change enthalpy of NPG/TAM is still larger than that of NPG. The component fraction has little effect on the phase change temperature of the binary systems. The decrease between the second phase change temperature of the binary system NPG/PE or NPG/TAM with the smaller NPG fraction and that of PE or TAM is large but the decrease between the first phase change temperature of NPG/PE or NPG/TAM with the larger NPG fraction and that of NPG is small, and therefore, the second phase change peak should be mainly considered in the binary system NPG/PE or NPG/TAM with the smaller NPG fraction, but the first peak should be mainly considered when the NPG fraction is larger.

2. It is better to prepare the experimental samples of polyalcohols by the way of crystallisation from ethyl alcohol which effectively prevents the volatilisation of the experimental samples during the process of preparation.
3. For the binary system with the larger NPG fraction, the second phase change peak is near the melting point, so it is better to use it in applications which have a working temperature lower than 40°C. When the NPG fraction is smaller, the first phase change enthalpy is too small, so it is better to use it in applications which have a working temperature higher than 140°C.

4. A little silicone oil in the binary system NPG/TAM effectively prevents the erosion of TAM to the aluminium container.
5. It is very important to seal the container, as polyalcohols vaporise severely if unsealed.
6. Graphite powder improves significantly the heat transfer of the binary systems of polyalcohols.
7. Supercooling is observed in the experiments. The maximum supercooling observed is 13.5°C. As the smallest rate of cooling in the experiments is 0.2°C/min, which is much larger than that of the natural cooling rate at the room temperature, it is expected that supercooling will be improved significantly if the material is cooled naturally.

4. Conclusions

In this work, an experimental study was conducted to investigate the heat storage performance of solid–solid phase change materials, including the binary systems of NPG/PE and NPG/TAM, consisting of NPG (neopentyl glycol, $C_5H_{12}O_2$), PE (pentaerythritol, $C_5H_{12}O_4$) and TAM (trihydroxy methyl-aminomethane, $C_4H_{11}O_3N$). It is found that the second phase change peak should be mainly considered in the binary system NPG/PE or NPG/TAM with smaller NPG fractions but the first peak should be mainly considered when the NPG fraction is larger. When the NPG fraction is larger, it is better to use the second phase change enthalpy in applications which have a working temperature lower than 40°C, but for the smaller NPG fractions, the first phase change enthalpy is too small, so it is better to use it in applications which have a working temperature higher than 140°C. The effects of some important factors, such as sealing of the container, adding silicone oil and graphite powder into the mixture and the preparation techniques of the experimental samples are observed.

Acknowledgements

This work is jointly supported by the National Natural Science Foundation of China (No. 59466001), the Science Foundation of Yunnan Province, and the 2000 Outstanding Scholars Scheme of Yunnan Province for Prof. W. Lin.

References

[1] Ruan D, Zhang T, Zhang D, Liang S, Hu Q. Acta Energiae Solaris Sinica 1994;15(1):19.
[2] Xing D, Shi G, Ruan D, Huo L, Li D, Zhang T, Zhang D. Acta Energiae Solaris Sinica 1994;16(2):131.
[3] Benson DK, Burrows RW, Webb JD. Solar Energy Materials 1986;13:133.
[4] Benson DK, Chandra D. Solid-state phase change materials for thermal energy storage. US DOE Contract No. DE-AC02-83CH10093, 1985.
[5] Son CH. Solid–solid phase change materials as a space-suit battery heat storage medium. Ph.D. thesis, University of South Carolina, 1989.

[6] Son CH, Morehouse JH. ASME Journal of Solar Energy Engineering 1991;113:244.
[7] Zhang ZY, Yang ML. Thermochimica Acta 1990;169:263.
[8] Murrill E, Breed L. Thermochimica Acta 1970;1:239.
[9] Zhang ZY. Thermochimica Acta 1992;202:105.
[10] Font J, Muntasell J, Navarro J, Tamarit JL, Lloveras J. Solar Energy Materials 1987;15:299.
[11] Wang Q. Hydrogen bonds in organic chemistry. Tianjin: Tianjin University Press, 1993.
[12] Wang X. Study on the heat storage performance of the monophyletic and binary systems of NPG, PE and TAM. M.Sc. thesis, Yunnan Normal University, Kunming, 1997.