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Micromechanism of heat storage in a binary system of two kinds of polyalcohols as a solid–solid phase change material

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Abstract

Solid–solid phase change materials are promising heat storage media for many applications. Polyalcohols are the hot spot of recent study and utilizations. In this paper, we explore the micromechanism governing heat storage in the binary system of two kinds of polyalcohols as solid–solid phase change materials. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyalcohol; Micromechanism of heat storage; Solid–solid phase change material; Binary system

1. Introduction

Heat storage devices are key elements for efficient utilization of solar thermal energy. Compared to sensible heat storage, phase change heat storage has the advantages of larger energy storage density, smaller volume requirement of the storage device, higher efficiency, fixed temperatures for the heat absorbing and removal cycle, etc. At present, solid–liquid phase change materials are extensively studied and utilized as efficient heat storage media, but most

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of the solid–solid phase change materials are not given enough attention due to their smaller latent heat and higher phase change temperatures.

Solid–solid phase change heat storage is the process in which some solid materials absorb a great deal of heat at a fixed temperature when they transfer from a low symmetry crystal structure to a high symmetry one. During the process, the materials will store a great deal of heat, and this amount of heat can be removed reciprocally for re-use. Compared to solid–liquid phase change materials, solid–solid phase change materials have the advantages of smaller volume changes during the phase change process, no leakage problems, smaller erosion to the device and longer service life among others, although they also have the drawbacks of smaller latent heat and higher phase change temperatures which are undesirable for low temperature applications. In addition, some crystalline solids with carbon and hydrogen elements can reciprocally absorb and remove a great deal of heat when they change from one crystal structure to another, which makes these solid–solid phase change materials potentially efficient and promising heat storage materials.

At present, the promising solid–solid phase change materials are polyalcohols, polyethylenes, layered perovskites, etc. Among the polyalcohols, NPG ($C_5H_{12}O_2$, neopentyl glycol), PE ($C_5H_{12}O_4$, pentaerythritol) and TAM ($C_4H_{11}O_3N$, trihydroxy methyl-aminomethane), are the favorites [1–11]. It is found that these polyalcohols are heterogeneous at low temperatures, but when the temperatures rise to the solid–solid phase change temperatures, their molecules become homogeneously face-centered cubic crystals with high symmetry and absorb a great deal of hydrogen bond energy as the hydrogen bonds among these square-bridge type molecules break. Experiments show that the phase change of polyalcohols is first order and their Gibbs changes are zero [12]. Benson et al. [3,4] believe that the solid–solid phase change enthalpy in NPG or PE should be as follows

$$\Delta H = T_s \Delta S = nB_h + \Delta H_0, \tag{1}$$

where ΔH_0 is the contribution from the non-hydrogen bond to the enthalpy which can be estimated from the solid–solid phase change enthalpy of neopentane which does not contain –OH (about 2.6 kJ/mol), B_h is the average hydrogen bond energy which is about 9.7 kJ/mol for the polyalcohols NPG and PE and n is the average hydrogen bond number in every molecule which is related to N, the number of –OHs in every molecule, by the following equation

$$n = \frac{fN^2}{4}. \tag{2}$$

For NPG and PE, N is 4 and 2, respectively, and $f = 1$, therefore,

$$\Delta H = \Delta H_0 + \frac{N^2 B_h}{4}. \tag{3}$$

To obtain solid–solid phase change materials which have a larger range of phase change temperatures, which are beneficial for low temperature utilizations of solar energy, it is reasonable to combine, at a fixed molecule fraction, two or more polyalcohols together to form an alloy type mixture whose phase change temperature can then be adjusted to meet the requirement of the application [13]. There are already some good results on these kinds of mixtures [1–11]. Benson et al., Zhang et al., and Ruan et al. examined experimentally the solid–solid phase change temperatures and enthalpy of the binary system consisting of NPG and PE. Benson et al. believed that the mechanism of the solid–solid phase change in the binary system of polyalcohols is similar to that in the monophyletic system, which is governed by the crystal structure change, but no reasonable explanation has been found to explain the micromechanism of heat storage in the binary system of polyalcohols, which is what we will address in this work.

2. Experiments and analysis

2.1. Experimental results

We have obtained experimental results, as shown in Table 1, of the heat storage performance of the monophyletic systems of NPG, PE and TAM and the binary systems of NPG/PE and NPG/TAM as solid–solid phase change materials using DSC and DTG techniques [13]. In Table 1, T_1, T_2, H_1, and H_2 are the first and second solid–solid phase change temperatures and enthalpies, respectively.

2.2. Analysis

Suppose that the thermal energy of a solid is the oscillation of $3N$ oscillators with the same frequency. The energy level of the oscillator is $E_n = (n + 1/2)\hbar\omega$, and the degeneracy is 1. According to the statistical rules, the partition function Z is as follows

Table 1
Experimental results of performance of solid–solid phase change heat storage of the monophyletic systems of NPG, PE and TAM and binary systems of NPG/PE and NPG/TAM

Material	T_1 (°C)	T_2 (°C)	H_1 (J/g)	H_2 (J/g)
PE	185.4		339.55	
NPG	42.4		119.10	
TAM	132.4		295.61	
$NPG_{0.382}PE_{0.618}$	32.0	169.8	18.79	147.73
$NPG_{0.528}PE_{0.472}$	34.0	160.3	26.20	83.02
$NPG_{0.618}PE_{0.382}$	35.2		33.16	
$NPG_{0.764}PE_{0.236}$	37.0		46.14	
$NPG_{0.854}PE_{0.146}$	37.4		51.50	
$NPG_{0.910}PE_{0.090}$	36.6		68.15	
$NPG_{0.382}TAM_{0.618}$	35.6		27.08	
$NPG_{0.528}TAM_{0.472}$	36.1		43.64	
$NPG_{0.618}TAM_{0.382}$	36.6		62.19	
$NPG_{0.764}TAM_{0.236}$	37.7		75.29	
$NPG_{0.854}TAM_{0.146}$	38.1		121.03	
$NPG_{0.910}TAM_{0.090}$	38.6		143.30	

$$Z = \prod_{i=1}^{3N} \sum_{n} \mathrm{e}^{-\beta E_n} = \prod_{i=1}^{3N} \sum_{n} \mathrm{e}^{-\beta(n+1/2)\hbar\omega}. \tag{4}$$

As

$$1 + x + x^2 + x^3 + \cdots + x^n = \frac{1}{1-x}, \quad \text{for } -1<x<1, \tag{5}$$

if we set $x = \mathrm{e}^{-\beta\hbar\omega}$, then

$$Z = \prod_{i=1}^{3N} \sum_{n} \mathrm{e}^{-\beta(n+1/2)\hbar\omega} = \prod_{i=1}^{3N} \frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1-\mathrm{e}^{-\beta\hbar\omega}}. \tag{6}$$

$$\ell n\, Z = \sum_{n} -\frac{\beta\hbar\omega}{2} - \sum_{n} \ell n(1-\mathrm{e}^{-\beta\hbar\omega}) \tag{7}$$

$$S = K\left(\ell n\, Z - \beta\frac{\partial}{\partial\beta}\ell n\, Z\right) = \sum_{n}\left[\hbar\omega\frac{\mathrm{e}^{-\hbar\omega/KT}}{T - T\mathrm{e}^{-\hbar\omega/KT}} - K\ell n(1-\mathrm{e}^{-\hbar\omega/KT})\right] \tag{8}$$

From experiments, we know that the thermal capacity of most materials will reach the classic value at room temperatures which makes us believe that the frequency of the lattice is much lower than that of the molecules.

Set $\theta_E = \hbar\omega/K$, at high temperatures, $T> >\theta_E$. Hence, $(1-\mathrm{e}^{-\hbar\omega/KT}) \to \hbar\omega/KT$, then

$$S = 3NK - \frac{3N\hbar\omega}{T} - 3NK\ell n\left(\frac{\hbar\omega}{KT}\right) \tag{9}$$

ω is related to the temperature and the bond strength. When the temperature increases, ω increases and when the bond strength increases, ω also increases. Solid–solid phase change occurs at a fixed temperature, and therefore, the entropy change during the phase change is as follow

$$\Delta S = S_1 - S_2 = 3NK\ell n\left(\frac{\omega_2}{\omega_1}\right) + \frac{3N\hbar(\omega_2-\omega_1)}{T}. \tag{10}$$

Suppose $\bar{\omega}$ and $\bar{\omega}'$ are, respectively, the average frequency of the molecules of the monophyletic and binary systems of polyalcohols and ΔS and $\Delta S'$ are, respectively, their corresponding entropy changes. From experiments, we know, $\Delta S - \Delta S' > 0$, that is,

$$\Delta S - \Delta S' = 3NK\ell n\left(\frac{\bar{\omega}_2}{\bar{\omega}_1}\right) + \frac{3N\hbar(\bar{\omega}_2-\bar{\omega}_1)}{T} - 3NK\ell n\left(\bar{\omega}\frac{'_2}{\bar{\omega}}{}'_1\right) + \frac{3N\hbar(\bar{\omega}'_2-\bar{\omega}'_1)}{T}$$
$$> 0 \tag{11}$$

After the phase change, NPG, PE and TAM all have the face centered cubic crystal structure, and there are very small differences among their, lattice constants. In this case, all the hydrogen bonds formed by –OH(–NH_2) among the molecules break down. Hence, if we ignore the difference between the average oscillation frequency of the monophyletic and binary systems of polyalcohols, i.e., $(\bar{\omega}'_2 - \bar{\omega}'_1) = 0$ from Eq. (8), we can find that $\bar{\omega}'_1 > \bar{\omega}_1$, that is, the average oscillation frequency of the molecules in the binary system is larger than that in the monophyletic systems before the phase change. However, from the experiments, we know that the solid–solid phase change temperatures of the binary systems are lower than those of the monophyletic systems. Therefore, the bond strength which holds the atoms in the molecules of the binary systems is larger than that of the monophyletic systems before the phase change, but for the hydrogen bonds, it is just the opposite.

When we discuss the crystals in which the bonds holding the atoms in the molecules are van der Waal bonds, the atom pair's interactive potential is usually used. The most popular potential is the Lainade–Qioosi potential, that is, $V(r) = A_n/r^n - A_m/r^m$. For the standard Lainade–Qioosi potential, $m = 6$, $n = 12$, A_n and A_m can be determined by the lattice constants and the values of the sublimation energy.

For the hydrogen bonds in NPG, the potential and force are as follows

$$V_1(r) = \frac{A_{1n}}{r^n} - \frac{A_{1m}}{r^m} = \frac{A_{1n}}{r^{12}} - \frac{A_{1m}}{r^6} \tag{12}$$

$$F_1(r) = -V'_1(r) = 12\frac{A_{1n}}{r^{13}} - 6\frac{A_{1m}}{r^7} \tag{13}$$

$$F'_1(r) = -156\frac{A_{1n}}{r^{14}} + 42\frac{A_{1m}}{r^8} \tag{14}$$

For the hydrogen bonds in PE, the potential and force are as follows

$$V_2(r) = \frac{A_{2n}}{r^n} - \frac{A_{2m}}{r^m} = \frac{A_{2n}}{r^{12}} - \frac{A_{2m}}{r^6} \tag{15}$$

$$F_2(r) = -V'_2(r) = 12\frac{A_{2n}}{r^{13}} - 6\frac{A_{2m}}{r^7} \tag{16}$$

$$F'_2(r) = -156\frac{A_{2n}}{r^{14}} + 42\frac{A_{2m}}{r^8} \tag{17}$$

From experiments, we know that the sublimation energy of PE is larger than that of NPG, but its lattice constants are smaller. Hence, $A_{2n} < A_{1n}$, $A_{2m} > A_{1m}$. When r is a little away from the equilibrium points, the changes of potential and force in PE are both larger than those in NPG.

Hence, we put forward the following hypothesis to account for the solid–solid phase change in the binary system of polyalcohols:

1. At low temperature, NPG, PE and TAM all have layered structures. Within the same layer, all the molecules are connected by hydrogen bonds and all –OH or –NH_2 in the molecules form hydrogen bonds among the molecules, and they connect with each other in a square

structure. For example, in Figs. 1 and 2, it can be found that the molecules of NPG or PE connect with each other in a square structure.

2. After PE or TAM is added into NPG, as all of them have different numbers of –OH in each molecule, the mixture can not be totally congruently melted and some molecules of one kind of polyalcohol randomly take the places of another kind which results in two kinds of substitutional solid solution crystals. In Fig. 3, it can be seen that the square structure hydrogen bond bridges in these crystals are also affected, and the structure may become the △ type or the – type.
3. The bond length of the △ or the – structure hydrogen bonds caused by the different numbers of –OH or $-NH_2$ in different molecules is larger than that of the square structure hydrogen bonds, which makes the bond energy smaller and the bonds easier to break. As when the length of the hydrogen bonds changes, the changes of potential and force in PE are larger than that in NPG, and therefore, the molecules of NPG take the places of PE or TAM in the crystal, which results in severe changes of the square structure hydrogen bond bridges and bigger changes of the hydrogen bond energy.

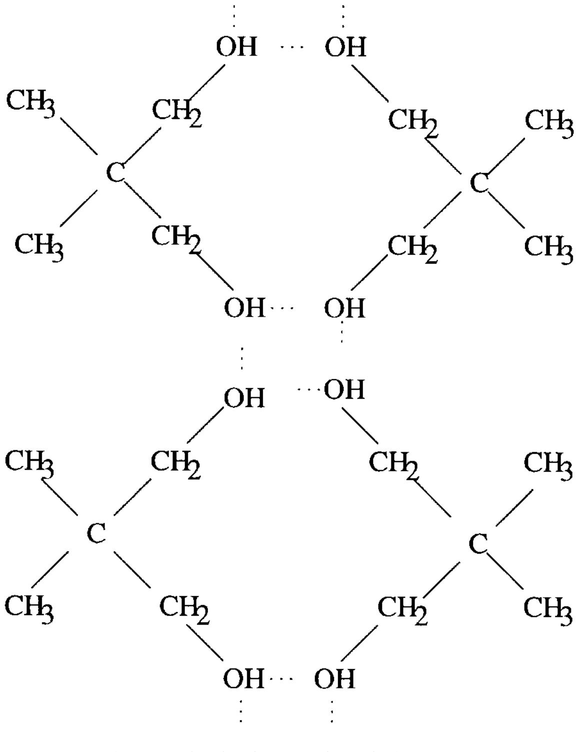

Fig. 1. The hydrogen bonds in NPG.

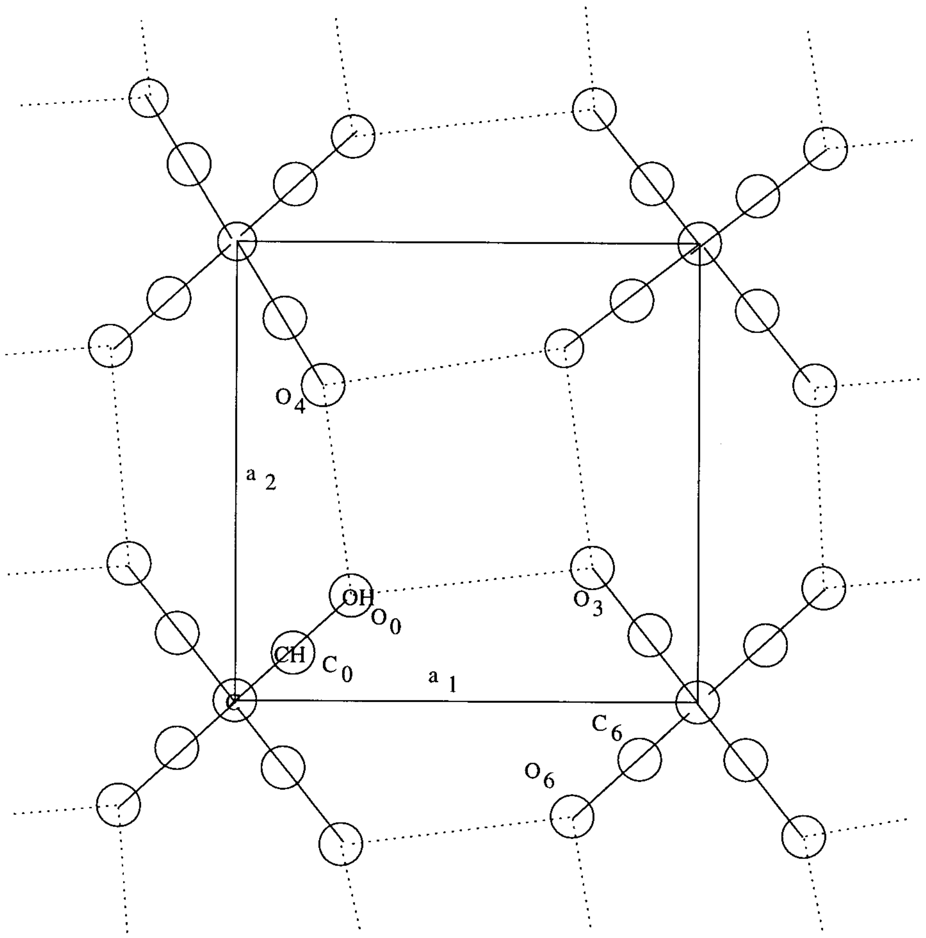

Fig. 2. The hydrogen bonds in PE.

3. Explanation to experimental phenomena

With the above hypothesis, we can account for some experimental phenomena:

1. The binary system of polyalcohols consists of two kinds of substitutional solid solution crystals, which results in two solid–solid phase change peaks in the same system. For the binary system of NPG/PE or NPG/TAM, the first solid–solid phase change temperature of the system is lower than that of the monophyletic system of NPG, but the second is lower than that of the monophyletic system of PE or TAM. As the lower phase change temperature of the binary system is caused by the change of hydrogen bond length, which is the result of place-taking of another polyalcohol molecule in this one, and the change of length of the hydrogen bonds is only related to the crystal structure of the polyalcohols, the solid–solid phase change temperature of the binary system has little relation with the molecule fraction of the two constituents in the system. When the molecule fraction of NPG

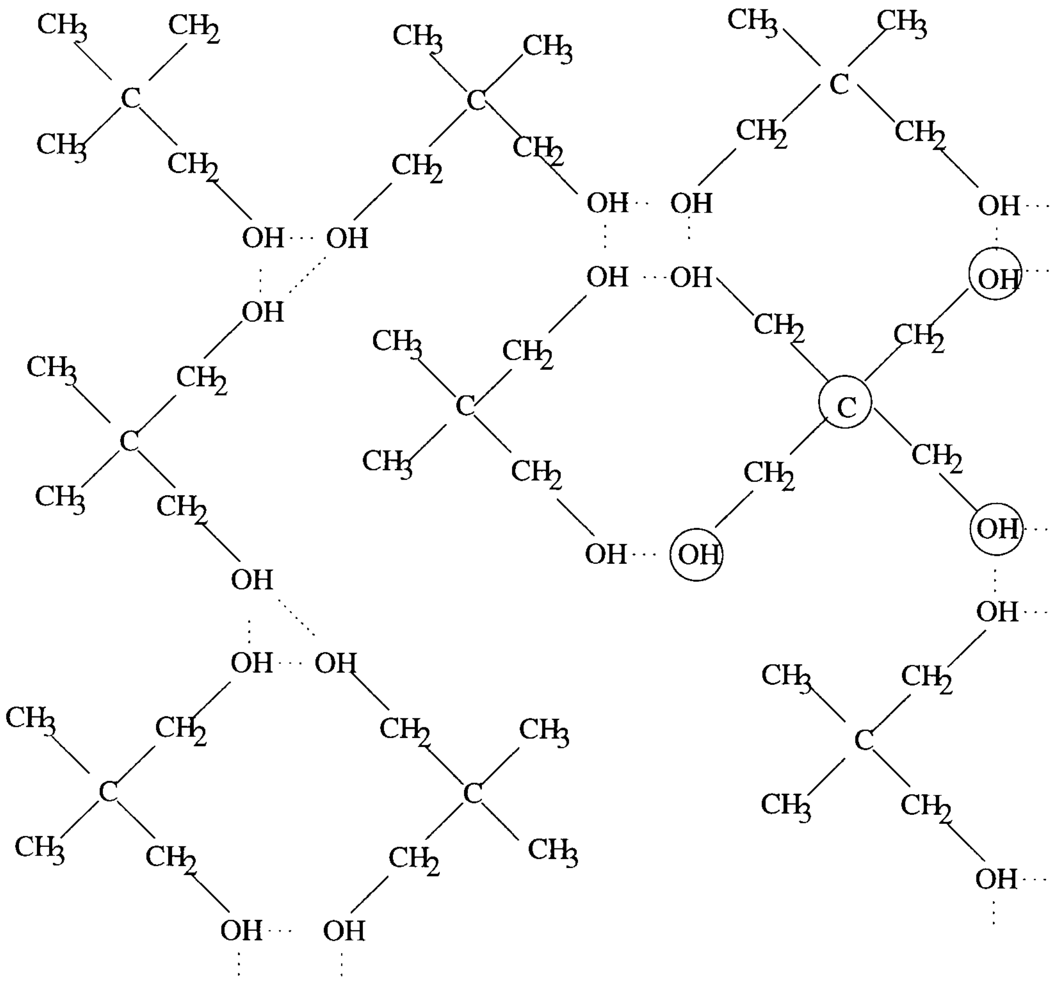

Fig. 3. The hydrogen bonds in the binary system of NPG/PE after PE is added into NPG.

increases, the number of deformed hydrogen bonds increases. At the temperature lower than the solid–solid phase change temperature of the monophyletic system which has the larger fraction, the number of hydrogen bonds which probably break down increases, which makes the other hydrogen bonds more easily broken down, and hence, with the increase of the molecule fraction of the major polyalcohol, the solid–solid phase change temperature relating to it in the binary system decreases a little.

2. As there are different numbers of hydroxyls between the molecules of the two constituents, the structure of the hydrogen bond bridges changes which makes some –OH or $-NH_2$ not form hydrogen bonds, and then, the hydrogen bond energy becomes smaller. Hence, the sum of the two solid–solid phase change enthalpies of the binary system is smaller than the sum of the monophyletic systems of the two constituents. In the binary system of NPG/PE, where NPG is the major constituent, although the PE taking the places in NPG will cause a

larger probability to form hydrogen bonds, the hydrogen bond energy will become too small, which results in the first solid–solid phase change enthalpy of the binary system being smaller than that of the monophyletic system of NPG. Similarly, the second enthalpy of this binary system is smaller than that of the monophyletic system of PE. In the binary system of NPG/PE, where PE is the major constituent, the lattice replacement of PE by NPG in the crystal not only decreases the probability of forming hydrogen bonds but also makes the change of hydrogen bond energy larger, and therefore, the amount of decrease between the second enthalpy of the binary system and that of the monophyletic system of PE will be larger than that between the first enthalpy of the binary system and that of NPG. As the hydrogen bond energy among the TAM molecules is smaller than that of the PE molecules, the replacement by TAM molecules in the NPG crystal will result in a smaller decrease of hydrogen bond energy and a bigger probability to form hydrogen bonds, and therefore, the first enthalpy in the binary system of NPG/TAM is larger than that in the binary system of NPG/PE with the same constituent fraction. Even when the molecule fraction of NPG is 0.854, the solid–solid phase change enthalpy of the binary system of NPG/TAM is larger than that of NPG.

3. The decrease of the second solid–solid phase change temperature of the binary system of NPG/PE or NPG/TAM is larger than that of PE or TAM, but the decrease of the first solid–solid phase change temperature of the binary system is smaller than that of NPG, which is caused by the bigger change of the force and length of the hydrogen bonds in the binary system.
4. In the binary system of NPG/PE with lower (or higher) fraction of NPG, PE (or NPG) is the major constituent and the second solid–solid phase change is more important. With the increase of the fraction of NPG (or PE), the square structure hydrogen bond bridges in PE will be affected more by NPG, which results in bigger deformation, and therefore, the second (or first) solid–solid phase change temperature of the binary system will be lower.

4. Summary

We have explored the micromechanism governing heat storage in the binary system of two kinds of polyalcohols as solid–solid phase change materials. Firstly, we make an analysis of the experimental results. Secondly, we put forward an hypothesis from the statistical view and, finally, account for the experimental phenomena with the hypothesis.

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