

Alcohols as a Phase Change Material with Excellent Thermal Storage Properties in Buildings

Dehong Li, Yuchen Chen, Alireza Kaboorani, Denis Rodrigue, Xiaodong (Alice) Wang

Abstract—Utilizing solar energy for thermal energy storage has emerged as an appealing option for lowering the amount of energy that is consumed by buildings. Due to their high heat storage density, non-corrosive and non-polluting properties, alcohols can be a good alternative to petroleum-derived paraffin phase change materials (PCMs). In this paper, ternary eutectic PCMs with suitable phase change temperatures were designed and prepared using lauryl alcohol (LA), cetyl alcohol (CA), stearyl alcohol (SA) and xylitol (X). The Differential Scanning Calorimetry (DSC) results revealed that the phase change temperatures of LA-CA-SA, LA-CA-X, and LA-SA-X were 20.52 °C, 20.37 °C, and 22.18 °C, respectively. The latent heat of phase change of the ternary eutectic PCMs were all stronger than that of the paraffinic PCMs at roughly the same temperature. The highest latent heat was 195 J/g. It had good thermal energy storage capacity. The preparation mechanism was investigated using Fourier-transform Infrared Spectroscopy (FTIR), and it was found that the ternary eutectic PCMs were only physically mixed among the components. Ternary eutectic PCMs had a simple preparation process, suitable phase change temperature, and high energy storage density. They are suitable for low-temperature architectural packaging applications.

Keywords—Thermal energy storage, buildings, phase change materials, alcohols.

I. INTRODUCTION

TO overcome the global energy shortage, new methods of energy storage and management need to be found. Recent studies reported that more than 40% of the energy generated worldwide is consumed in buildings [1]. Therefore, the key to managing and controlling energy storage is lowering building energy consumption. In this regard, new solutions are needed to maintain constant indoor temperatures to reduce the energy related to heating, ventilation and air conditioning systems.

PCMs are promising for a wide range of applications in building thermal engineering due to their unique properties: high thermal energy storage density and low phase change temperature during the charging and discharging process [2], [3]. The phase transition model classifies PCMs into four categories: solid–gas, solid–liquid, solid–solid and liquid–gas [4]. Solid–gas PCMs and liquid–gas PCMs involve significant volume changes during phase transformation, necessitating higher containment requirements and fewer applications in practice [5]. Nevertheless, the volume change associated with solid-solid PCM during the transition is small. However, the

disadvantage of small latent heat of phase change and large subcooling level leads to low energy storage efficiency. Therefore, it is not highly used in practice [6]. By utilizing endothermic and exothermic events during the melting and solidification processes, solid-liquid PCMs can store and release heat energy. The enthalpy of phase change is high, while the volume change is low during the solid-liquid phase transition. The phase change process is very slow and simple to manage [7]. Solid-liquid PCMs have been developed into the most intriguing category of PCMs due to their advantages. Fig. 1 illustrates the solid-liquid PCMs' operational method. The material changes from a solid to a liquid throughout the day and absorbs thermal energy when the ambient temperature is higher than the phase transition temperature. Then, the material converts from liquid to solid to release heat at night when the outside temperature is below the phase transition point, keeping the interior temperature at a comfortable level [8].

The most popular solid-liquid phase change compound used today in construction is paraffin. It has been widely commercialized because of its wide range of phase change temperature, high thermal energy storage density, low volume change during the phase change process, low vapor pressure, and low cost [4]. However, the ideal PCMs should have not only good thermophysical, chemical and economic properties, but also good environmental performance. The extensive usage of paraffin phase transition material not only increases energy consumption, but also causes several environmental issues because paraffin wax is made from non-renewable petroleum resources. Therefore, the ideal solution is to develop a sustainable PCM to replace paraffin wax while still having its advantages.

One possibility are alcohols which are bio-based materials having high energy storage density. Vivekananthan and Amirtham [9] prepared a composite PCM with high thermal conductivity (1.122 W/(m·K)) by adding 1% graphene to erythritol. However, the phase change temperature was very high (117.8 °C) which is not suitable for low temperature building applications. Zhou et al. [10] prepared a xylitol PCM containing 10 wt% of expanded graphite by impregnation and compression. The thermal conductivity was high (3.91 W/m·K), while the phase change occurred at 93.3 °C. Li et al. found that the phase change temperature of LA was 24 °C, while that of SA was 58 °C and Dulcitol underwent phase

Dehong Li, Yuchen Chen, and Xiaodong (Alice) Wang are with the Department of Wood and Biomass Materials Engineering, University Laval, Quebec, QC G1V0A6 Canada (e-mail: dehong.li.1@ulaval.ca, yuchen.chen.1@ulaval.ca, xiaodong.wang@sbf.ulaval.ca).

Alireza Kaboorani is with the Building Efficiency Technology Access

Centre, Red River College, Winnipeg, MB R3H0J9 Canada (e-mail: akaboorani@rrc.ca).

Denis Rodrigue is with the Department of Chemical Engineering, University Laval, Quebec, QC G1V0A6 Canada (e-mail: denis.rodrigue@gch.ulaval.ca).

change at 185 °C. So most of the alcohol-based PCMs undergo phase changes in the medium to high temperature range [4]. However, Hu et al. found that the optimal thermal comfort temperature for the human body is 17.3-22 °C [11].

In this study, based on the second law of thermodynamics and phase equilibrium theory, ternary eutectic PCMs with suitable phase change temperatures were prepared using LA as the basic component.

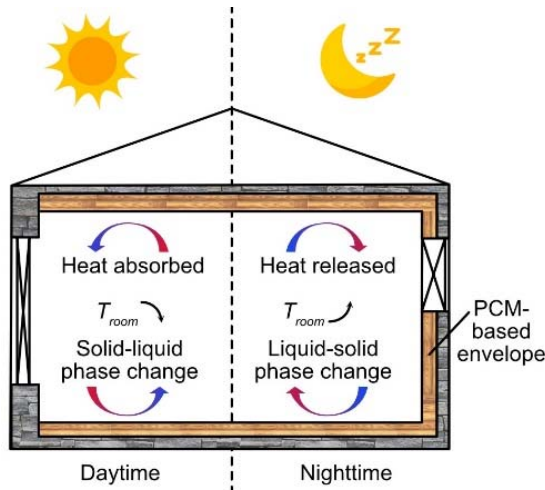


Fig. 1 The working mechanism of PCMs for building encapsulation

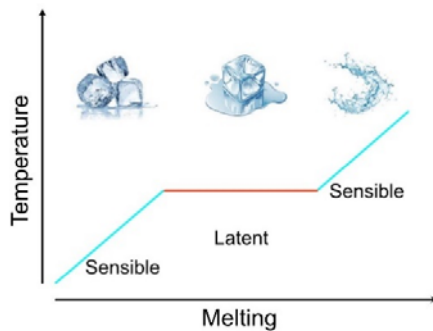


Fig. 2 Diagram of the process of energy management by PCMs

II. THERMAL ENERGY STORAGE TECHNOLOGY

Building energy management is crucial. It can cut down on both energy use and the costs of keeping indoor spaces comfortable. Energy efficiency and energy management are closely related. Enhancing energy efficiency will offer a practical means of lowering greenhouse gas emissions (GHG) [12]. The process of energy management of PCMs is shown in Fig. 2. This process consists of three parts. The first and last part is sensible heat storage and the second part is latent heat storage [13]. The sensible heat is stored by increasing the temperature of the thermal storage medium. On the other hand, latent heat storage takes advantage of the fact that materials require a large amount of heat when they melt; they absorb a high amount of heat to convert from a solid to a liquid state. Studies have shown that the heat storage capacity of a latent heat medium is 5-14 times that of a sensible heat medium [14]. So, the focus should be on the development of latent heat

thermal energy storage as an effective way to save thermal energy.

III. MATERIALS AND METHODS

A. Materials

LA (23.99 °C, 200 J/g), CA (49.93 °C, 228 J/g), SA (58.85 °C, 228 J/g) and xylitol (X, 94.41 °C, 242 J/g) were purchased from the Sigma-Aldrich chemical company (USA) and used as received.

B. Eutectic Temperature and Latent Heat Calculation Methods

Eutectic PCMs are special mixtures of two or more substances with different melting points. A eutectic mixture has a lower melting point than any of its component [15]. According to the second law of thermodynamics and phase equilibrium theory, the melting temperature and latent heat of eutectic PCMs can be calculated by the following equations [16], [17]:

$$T_m = \frac{1}{\frac{1}{T_i} + \frac{R \cdot \ln(X_i)}{\Delta H_i}} \quad (1)$$

where T_m is the melting temperature of eutectic PCMs (K); T_i is the melting temperature of component i (K); R is the gas constant (8.314 J/mol·K). X_i is the mole fraction of component i ; ΔH_i is the melting latent heat of component i .

$$H_m = T_m \sum_{i=1}^n \frac{X_i H_i}{T_i} \quad (2)$$

where H_m is the melting latent heat of eutectic PCMs.

C. Preparation Method of Ternary Eutectic PCMs

The preparation of ternary eutectic PCMs is shown in Fig. 3. Firstly, each PCMs component was weighed according to the calculated eutectic molar ratio and added to a 100 mL beaker, separately. LA, CA, SA and xylitol were heated at 40 °C, 60 °C, 70 °C and 110 °C until they were completely melted to a liquid state, respectively. Finally, the components were mixed (mechanical stirring) and heated at 40 °C for 0.5 h at a speed of 500 rpm. The eutectic mixture was finally collected for testing.

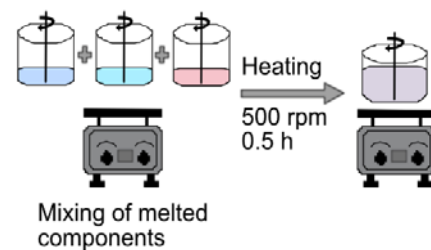


Fig. 3 Preparation process of ternary eutectic PCMs

D. Characterization Method of Differential Scanning Calorimetry

Differential scanning calorimeter (Q1000, TA instruments, USA) was used to determine the melting temperature and latent

heat of eutectic PCMs. The samples were first heated to 40 °C to eliminate the thermal history; then, cooled down to 0 °C and finally reheated to 40 °C. The melting temperature and latent heat were determined from the second heating step. The heating/cooling rate was fixed at 10 °C/min.

E. Characterization Method of FTIR

The samples were first dried in an oven at 50 °C for 12 h. A FTIR (INVENIO R, Bruker Corporation, USA) was used to analyze the samples. The test parameters are a resolution of 4 cm⁻¹ for 32 scans between 4000 and 400 cm⁻¹.

IV. RESULTS AND DISCUSSION

A. Thermal Storage Properties of Eutectic PCMs

The preparation method for eutectic mixtures to obtain new PCMs of suitable temperature was investigated. First, the eutectic phase change temperature and the eutectic latent heat were calculated for any two components. Then, the binary eutectic PCM was considered as one component, and the phase change temperature and latent heat of phase change of the ternary eutectic PCM were calculated together with the addition of the third component. According to (1) and (2), the theoretical molar ratio, eutectic temperature and latent heat of ternary eutectic PCMs are reported in Table I. The theoretical eutectic temperatures of the ternary eutectic PCMs exhibited different degrees of reduction. The theoretical melting temperatures of LA-CA-SA, LA-CA-X and LA-SA-X PCMs were reduced by 3.85 °C, 3.62 °C and 1.81 °C respectively, compared to pure LA. All of them have high latent heat (above 150 J/g) and are suitable for building encapsulation applications.

TABLE I
THEORETICAL EUTECTIC TEMPERATURE AND LATENT HEAT OF TERNARY PCMS

Materials	Molar Ratio	Theoretical Temperature (°C)	Theoretical Latent Heat (J/g)
LA-CA-SA	83:12:5	20.14	154
LA-CA-X	84:12:5	20.37	156
LA-SA-X	83:12:5	21.72	169

The ternary eutectic PCMs prepared according to the theoretical molar ratio with the alcohol fraction used are shown in Fig. 4 (a). The LA-CA-SA and LA-CA-X PCMs were liquid when the PCMs were at room temperature (22 °C). This indicates that they can undergo phase change below 22 °C. LA-SA-X PCM contains both liquid and solid states, indicating that it undergoes partial melting. LA, CA, SA and X all show solid forms as they do not reach the required phase transition temperature. But all of them melted to liquid by heating up to 95 °C. Fig. 4 (b) shows that all the prepared ternary PCMs had no significant layering, indicating a good compatibility between the components. The actual phase transition temperatures and latent heat of the ternary eutectic PCMs were finally determined via DSC and the results are shown in Fig. 5. For example, the eutectic temperature of LA-CA-SA PCM is 20.52 °C. This is very close to room temperature and the difference with the theoretical eutectic temperature is less than 2%. This confirms that the theoretical predictions were very good (accurate). But

the latent heat was higher than the predicted value, reaching 185 J/g. LA-CA-X PCM underwent a phase transition at 20.37 °C, which was consistent with the theoretical eutectic temperature. The eutectic latent heat was 195 J/g, which was about 75 J/g higher than that of the widely used paraffin PCM with a phase transition temperature of 20.37 °C [18]. The melting temperature of LA-SA-X PCM was 22.18 °C which represents only a difference of 0.46 °C from the theoretical value. The latent heat of phase change was as high as 176 J/g. So, all the prepared ternary eutectic PCMs can undergo phase transformation around the optimal human thermal comfort range and all of them have high thermal storage properties. So, they can be used as a good substitute for paraffin PCMs in architectural encapsulation applications.

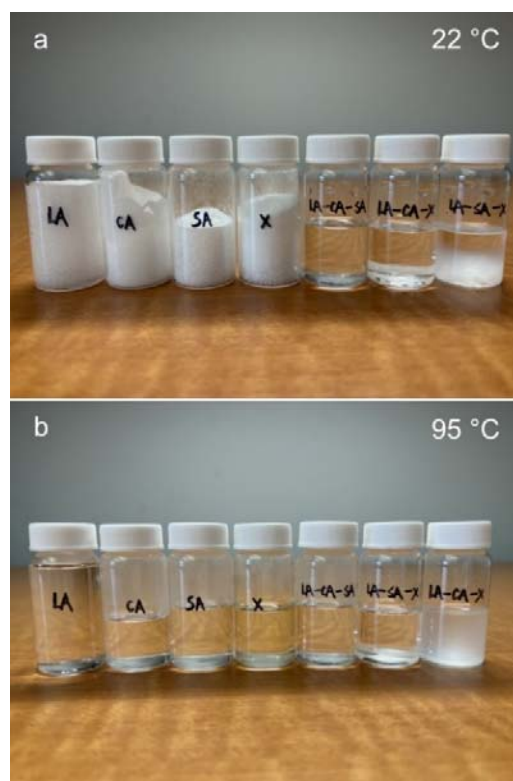


Fig. 4 Melted ternary eutectic PCMs

B. Preparation Mechanism of Eutectic PCMs

The molecular structure and chemical composition of the sample can be analyzed using FTIR spectroscopy. The infrared spectra of the ternary eutectic PCMs are shown in Fig. 6. The specific peaks are reported in Table II. Since the raw materials used were all alcohols, the FTIR spectra had similar peak shapes. The broad absorption peak near 3308 cm⁻¹ is due to the stretching vibration of the OH group of the alcohol. The asymmetric stretching and symmetric stretching of methylene appeared at 2918 cm⁻¹ and 2850 cm⁻¹, respectively [19]. The mixed vibration of OH is located at 744 cm⁻¹ [20]. Finally, the peak at 1064 cm⁻¹ is attributed to the stretching vibration of C-O [19]. An analysis of the spectra of the prepared ternary eutectic PCMs revealed that no peak disappeared nor new peaks were generated compared to the raw material. This indicates

that the preparation of the ternary eutectic PCMs did not involve a chemical reaction; i.e. it was only a purely physical mixture.

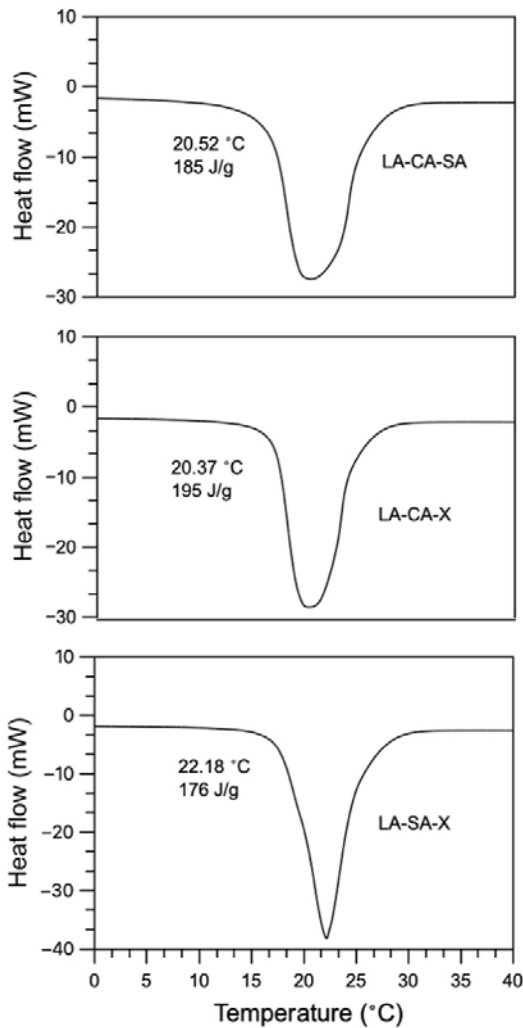


Fig. 5 DSC curves of the ternary eutectic PCMs

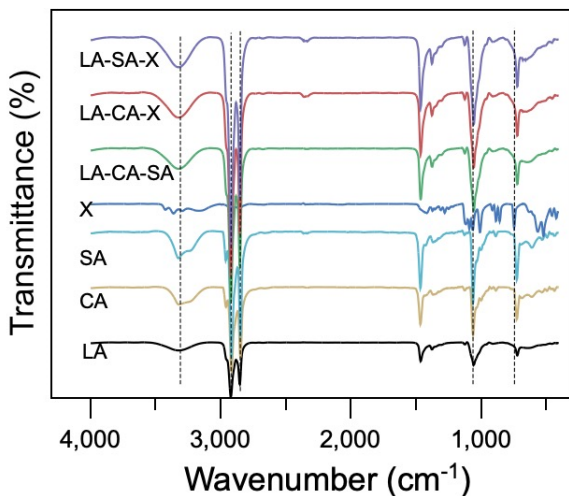


Fig. 6 FTIR spectra of ternary eutectic PCMs

TABLE II
 PEAKS ASSIGNMENT FOR FTIR SPECTRA OF TERNARY EUTECTIC PCMS [19], [20]

Wave Number (cm ⁻¹)	Vibrational Mode
3308	v(O-H)
2918	v _{as} (CH ₂)
2850	v _s (CH ₂)
1064	v(C-O)
744	v(O-H)

V. CONCLUSION

In summary, the thermal storage capacity and preparation mechanism of ternary eutectic PCMs were investigated. Three ternary eutectic PCMs were prepared by mixing after melting. The following are the study's main findings:

- 1) The ternary eutectic PCMs LA-CA-SA, LA-CA-X, and LA-SA-X had good compatibility among the components and underwent phase change at 20.52 °C, 20.37 °C and 22.18 °C, respectively. The theoretical phase transition temperature was in good agreement with the measured phase transition temperature via DSC. The latent heat of phase change ranged from 176 J/g to 195 J/g, which were slightly higher than the predicted values. Nevertheless, all the PCMs had higher thermal storage capacity than paraffin wax.
- 2) No chemical reaction occurred between the components of the prepared ternary eutectic PCMs. The preparation process was a simple physical mixing.
- 3) The developed ternary eutectic PCMs had high latent heat (above 150 J/g) and appropriate phase change temperature (around 21 °C) for use in building encapsulation.

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