# Preparation and Characterization of Neopentyl Glycol/Epoxy Resin Shape-Stabilized Phase Change Material for Thermal Energy Storage

**Duo Meng, Kang Zhao, Anqi Wang and Wei Zhao**

School of Civil and Architectural Engineering, Liaoning University of Technology, No.169 Shiying Street, Guta District,  Jinzhou, China

Email: mengduo39@163.com

**Abstract.** Neopentyl glycol is a kind of solid-solid phase change material for thermal energy storage. In order to overcome volatilization weight loss caused by the high saturated vapor pressure of neopentyl glycol，epoxy resin was chosen as the encapsulation matrix to inhibit the volatilization of neopentyl glycol when it happens phase change or works in a relatively high temperature environment. The micro morphology analysis indicated that the neopentyl glycol was encapsulated evenly in the epoxy resin matrix. These two components had no chemical reactions and combined with each other by the physical encapsulation. Phase change temperature and latent heat of the composite was measured as 41.26℃ and 57.04 J/g respectively，which proves the thermal heat storage performance of the neopentyl glycol was not influenced by the adding of epoxy resin. Meanwhile, attributed to the effective encapsulation and protection by epoxy resin, volatilization weight loss of the neopentyl glycol in the composite decreased significantly and behaved good thermal stability and reliability. After 100 times thermal cycling test, the composite hardly changed in the thermo-physical properties. Thus, the prepared neopentyl glycol/epoxy resin composite phase change material is supposed to be a potential and promising functional material for the applications in low temperature building energy conservation and solar energy storage.

## 1. Introduction

Phase change materials (PCMs) are a kind of functional materials which have the ability to absorb and release thermal energy at a certain temperature range near their phase change temperature. PCMs working as energy storage carrier can improve the energy utilization efficiency and alleviate the energy crisis. Attributed to the advantages such as high efficiency, saving energy and environmental protection etc., PCMs have been applied widely in the fields of industrial waste heat utilization, solar energy utilization, building thermal energy storage and so on [1]. The commonly used PCMs include solid-liquid and solid-solid phase transition forms, and there have been many researches and applications about these two kinds of PCMs [2]. However, liquid leakage is always a fatal problem for the liquid-solid PCMs in the process of heat absorption. Therefore, a packaging container [3] or shape-stabilized matrix [4-6] would be needed to overcome this disadvantage. Polyol is kind of solid-solid PCMs which do not generate liquid while absorbing the latent heat. They have the advantages of wider phase transition temperature range, small volume change, non-toxic, non-corrosion and loose requirements for PCM container and operation conditions. The latent heat of polyol is comparative with that of the solid-liquid PCMs and the super-cooling degree is small [7]. So the polyol is suggested to be a kind of potential and promising PCMs in latent thermal energy storage systems [8-10].

The biggest problem of polyol is the higher saturated vapor pressure which can generate the volatilization of polyol in the relatively low working temperature range. The volatilization will cause the weight loss of polyol and its thermal storage capacity will be influenced resultingly. This is profitless to the long-term thermal stability and reliability in engineering application for the polyol PCMs. Taking neopentyl glycol (NPG) as an example, its saturated vapor pressure is about 3 Pascal. In the repeated heating/cooling cycling process or high temperature working environment, the NPG may volatize and leads to the weight loss and finally influence the latent heat storage and service life of NPG servicing as the thermal energy medium. One of the feasible methods is to choose an encapsulation matrix to inhibit the volatilization of NPG. So the objective of this paper was the preparation of NPG/epoxy resin (EP) composite as a thermal-stable composite PCM by incorporation of NPG within the EP to resist the volatilization weight loss of NPG. EP has tight structure and is able to keep solid and rigidity near the solid-solid phase change temperature of NPG. The characterizations of chemical structure, micro morphology, thermo-physical properties and thermal reliability of the NPG/EP composite PCM were examined by FT-IR, SEM and DSC techniques, Service performance. In addition, the influence of the weight loss improvement of the NPG/EP composite PCM was also evaluated experimentally.

## 2. Experimental

### 2.1. Materials
Neopentyl glycol (NPG) working as the phase change material was supplied by Tianjin Kemiou Chemical Reagent Co., Ltd. Epoxy resin (EP) of E-44 type which was supposed to be encapsulation matrix to NPG and modified amine curing agent of T-31 type were provided by Wuxi Bluestars Petrochemical Co., Ltd. Anhydrous ethanol and acetone acting as solvent in the preparation of NPG/EP composite PCM was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd.. The main physical parameters of E-44 EP are listed in Table 1.

**Table 1.** The Main Physical Parameters of EP

| Property | Quantity |
|---|---|
| Appearance | No visible impurities |
| Epoxy equivalent/ g·eq-1 | 210~244 |
| Viscosity /Pa·S | 6~10 |
| Softening point /°C | 12~20 |

### 2.2. Preparation of the NPG/EP Composite PCM
The melt blending method was conducted on the preparation of the NPG/EP composite PCM.

1) The NPG was dissolved in anhydrous ethanol firstly and irradiated by the infrared lamp until the anhydrous ethanol volatilized completely. After cooled to the room temperature, the NPG was poured into a mortar and grinded into powders. The dissolved raw material of EP was put into a drying oven for about 2 h at the temperature of 50°C and then cooled to the room temperature for use.

2) A certain amount of NPG was put in the acetone solution and dissolved completely at 50°C. The equal weight of NPG and EP was mixed together uniformly by stirring to be a mixture solution. Then the T-31 modified amine curing agent was dripped in the mixture at the ratio of 20wt% by EP. After agitated evenly, the mixture solution was poured into the stainless steel mold coated with release agent. The mold was vacuumized for 2 h and then cured at the room temperature for 96 h. In order to make the EP cure completely and remove the acetone solvent, the mold filled with NPG and EP was dried in the drying oven at 65°C for 1 h. When cured entirely, the sample was naturally cooled to the room temperature and then taken out of the mold.

3) The anhydrous ethanol was used to flush the composite PCM block for several times until its surface was clear, and the NPG/EP composite PCM was finally obtained after dried in the drying oven to make the anhydrous ethanol volatilize out.

## 2.3. Instruments and Measurements

Fourier-transform infrared (FT-IR) was carried out on a EQUINX55 spectrophotometer to investigate the compatibility and interaction between NPG and EP matrix. Scanning electronic microscope (SEM) observations were performed for the PCM samples on a JSM-5600LV microscope. Thermal properties such as latent heat and phase change temperature of pure NPG and NPG/EP shape-stabilized PCMs were obtained by using differential scanning calorimetry (DSC) instrument (DSC822$^e$, Mettler). The amples were heated from 10°C to 70°C at a heating rate of 5°C min$^{-1}$ in a static nitrogen atmosphere. Thermogravimetric (TG) analysis was subjected on a thermo-analyzer instrument (TGA/SDTA851$^e$, Mettler). The samples were treated in the instrument from atmosphere temperature to 700°C at a heating rate of 10°C min$^{-1}$ in a static nitrogen atmosphere.

## 2.4. Thermal Cycling Test

For investigating the variation of thermo-physical properties of the NPG/EP composite PCM after enduring many times phase transition, accelerated heating-cooling thermal cycling test was conducted on the composite PCM. In the thermal cycling test, the heating temperature was 60°C, while the cooling temperature was determined to be 0°C implemented in a refrigerator. The heating-cooling process was repeated for 100 times and DSC analysis was used for measuring the phase change temperature and latent heat of the NPG/EP composite PCM after the thermal cycling.

## 3. Results and Discussion

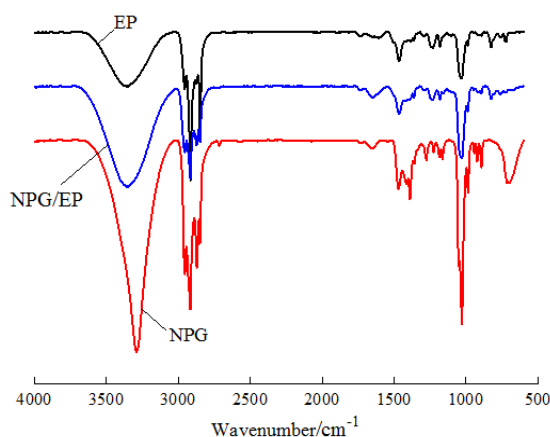### 3.1. Chemical Structure of the Composite PCM



**Figure 1.** FT-IR Spectra of the Samples

FT-IR spectra of EP and NPG/EP composite PCM are shown in Figure 1. From the infrared absorption spectrum of NPG, it can be seen that there are two obvious absorption peaks in the wavenumber of 2915.84 cm$^{-1}$ and 2848.34 cm$^{-1}$, which caused by the stretching vibration of C-H group. The overlapping peaks in 1465.64 cm$^{-1}$ and 1390.42 cm$^{-1}$ correspond to the bending vibration of C-H group. The peaks in 1274.72 cm$^{-1}$ and 1224.58 cm$^{-1}$ are the characteristic absorption peaks of -OH groups. As seen in the spectrum of EP in Figure 2, there is an absorption peak at 3355.53 cm$^{-1}$ which is caused by the stretching vibration of N-H. The characteristic peaks of C=C aromatic nucleus appear at the wavenumber of 1461.78 cm$^{-1}$ and 1589.1 cm$^{-1}$. From the FT-IR spectrum of NPG/EP composite in Figure 2, it is can be found that the typical peak of -OH in NPG has shifted to 1276.6 cm$^{-1}$ and 1226.71 cm$^{-1}$ respectively. The characteristic absorption peaks of C=C and C-H group both have appear, and the rest of the main characteristic peaks just have a little change in location and strength. Moreover, there are no new absorption peaks appear in the composite PCM. It is can be concluded that there are no chemical reactions between NPG and EP in the composite PCM. EP just plays a role in encapsulating NPG to confine its volatilization.

## 3.2. Morphology Analysis

For investigation the encapsulation effect of EP to NPG, the sectional microstructure of EP and NPG/EP composite PCM were observed by SEM respectively, shown in Figure 1. From the EP morphology of Figure 1(a), it can be seen that the surface of EP is smooth without any pores or particles and the structure is compact. Figure 2(b) shows the section microstructure of NPG/EG composite PCM. Compared with EP,   NPG/EP composite is less compact than EP and has a lot of pores ranging from 0.5 μm to 12.5 μm. A certain amount of NPG crystal particles are found in the relatively big pores, which illustrates that most of NPG are encapsulated in the supporting material of EP in the small molecules form. When the environmental temperature reaches to the phase change temperature of NPG, EP can encapsulate the NPG so well that the volatilization of NPG would be restrained effectively. Because the softening point of EP is much lower than the solid-solid phase change temperature of NPG, EP can prevent the weight loss of NPG caused by volatilization in the composite PCM. Thus, the composite PCM can maintain the good thermal storage performance for a long time in service.
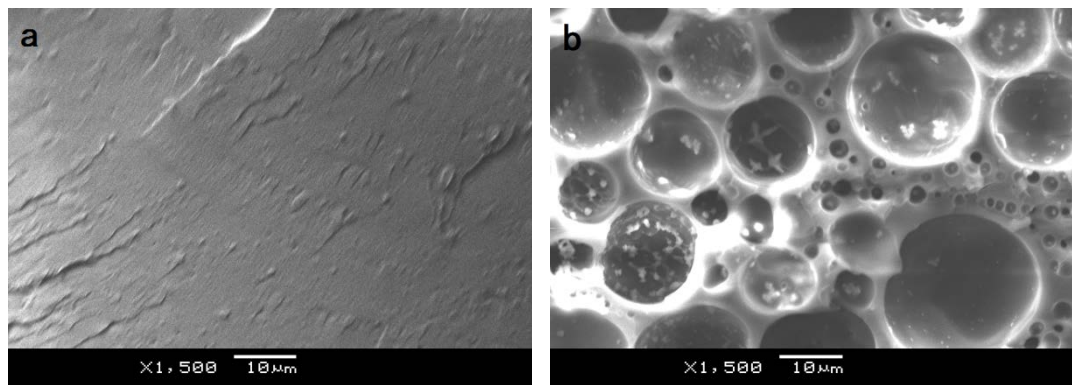


**Figure 2.** SEM Images: (a) EP; (2) NPG/EP Composite PCM

## 3.3. Thermo-Physical Properties of the Composite PCM

The important thermo-physical properties of PCMs including phase change temperature and latent heat were measured by DSC technique. Figure 3 illustrates the DSC curves of the NPG and NPG/EP composite PCM. In Figure 3，the DSC curve of NPG shows that the phase change temperature of NPG is 42.88°C and the latent heat is 115.1 J/g. As seen in the DSC curve of NPG/EP composite PCM, the phase change temperature of the composite is 41.26°C which is slightly lower than that of pure NPG. Due to no heat absorption behavior below 70°C of EP, the similar phase change temperature between NPG and NPG/EP composite indicates that the endothermic peak in the composite is only attributed to the phase change heat absorption of NPG. As a result, the latent heat of NPG/EP composite PCM is 57.04 J/g, which means that the mass fraction of NPG in the composite PCM is 49.6% based on Formula (1). The mass fraction of NPG in theory is 50% according to the preparation method, so it can be deduced that NPG has no loss during the reaction process with EP and maintains the intrinsic phase change thermal storage capacity. The FT-IR test results also verify that EP is only a supporting material and have little impact on the latent heat storage properties of NPG.

$$W_{NPG} = \frac{\Delta H_{NPG/EP}}{\Delta H_{NPG}} \tag{1}$$

Where $W_{NPG}$ is the mass fraction of NPG in NPG/EP composite PCM, %; $\Delta H_{NPG/EP}$ is the latent heat of NPG/EP composite PCM, J/g; $\Delta H_{NPG}$ is the latent heat of NPG, J/g.
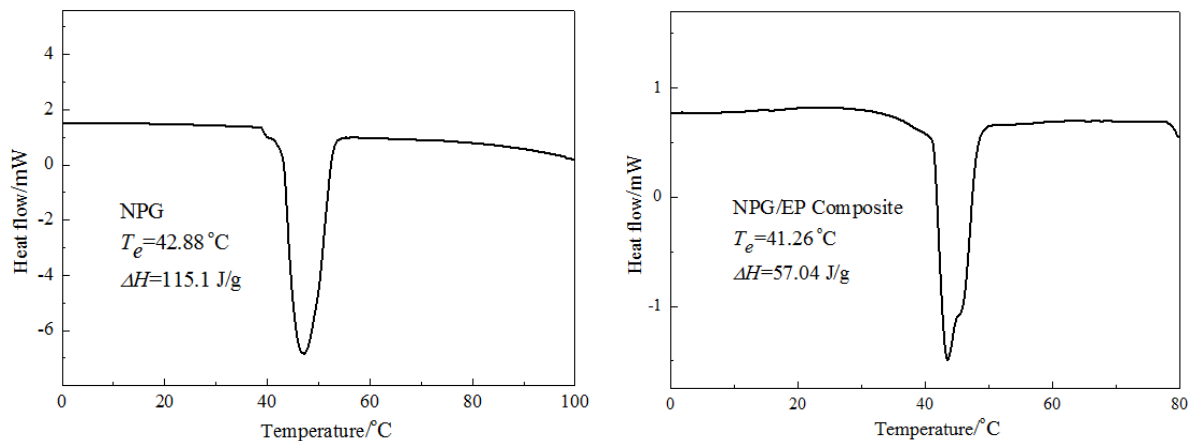
**Figure 3.** DSC Curves of NPG and NPG/EP Composite PCM

### 3.4. Volatilization Weight Loss of the Composite PCM

After NPG undergoing the repeated heating-cooling thermal cycling or working under a relatively high temperature environment, NPG may volatilize because of its higher vapor pressure. This will lead to the mass loss of NPG or NPG based composite PCMs, which affects the service performance in latent heat storage application of the PCMs. To examine the volatilization weight loss of the prepared NPG/EP composite PCM and the protection effect of EP to NPG, the weight loss variations were recorded by weighing the tested samples after heated to the temperature of 40℃, 60℃ and 100℃, respectively. The weight loss rates of NPG, EP and NPG/EP composite are shown in Table Ⅱ.

**Table 2.** The Weight Loss of PCMs at Different Temperature

| Material | Initial weight /g | Weight loss rate/% | | |
|---|---|---|---|---|
| | | *40℃* | *60℃* | *100℃* |
| NPG | 10 | 0 | 0.8 | 22.1 |
| EP | 10 | 0 | 0 | 0 |
| NPG/EP | 10 | 0 | 0.05 | 3.25 |

From the results in Table Ⅱ, it can be known that EP has no weight loss in the three heating processes. Pure NPG has no weight loss either after it was heated to 45℃ and happened solid-solid phase transformation. However, when heated to 60℃, the weight of NPG has decreased by 0.8% because of the volatilization. While heated to 100℃, the weight of NPG decreased significantly, by 22.1%. Due to EP having no weight loss below 100 ℃, the weight loss of the NPG/EP composite PCM is caused only by NPG. As can be seen, the weight loss rate is only 0.10% at the temperature of 60 ℃ and 6.5% at 100 ℃. By the comparison, it is obvious that the EP has remarkably suppressed the volatilization of NPG and improves the thermal stability of the NPG/EP composite PCM. The prepared NPG/EP composite PCM in our research is supposed to be used in the field of low temperature building energy conservation applications and the designed work temperature is less than 60 ℃. While the composite PCM hardly has weight loss below 60℃ proved by the test, as a result, the engineering application of this kind of NPG/EP composite PCMs is feasible.

### 3.5. Thermal Reliability of the Composite PCM

DSC curve of the NPG/EP composite PCM subjected 100 times accelerated heating-cooling thermal cycling test is given in Figure 4. As shown in Figure 4, the phase change temperature of the NPG/EP composite PCM is 41.13℃, being similar to the initial phase change temperature of NPG and the NPG/EP composite. Its latent heat is 55.97 J/g, which is reduced by1.88% than that of NPG/EP composite PCM before thermal cycling. According to the results in 3.4, the NPG/EP composite PCM

happened mass loss at the heating temperature of 60°C ascribed to the volatilization of NPG completely. So after the repeated thermal cycling treatment, the heat storage capacity of the composite PCM would decline. On the basis of DSC result in Figure 4, however, the mass loss rate of the composite PCM has no directly proportional relationship to the thermal cycling times on the composite PCM. The latent heat of NPG/EP composite changes small and this change can be neglected in the engineering application. Moreover, the slight mass loss is able to be alleviated even avoided by using a reasonable application means or advanced construction method.
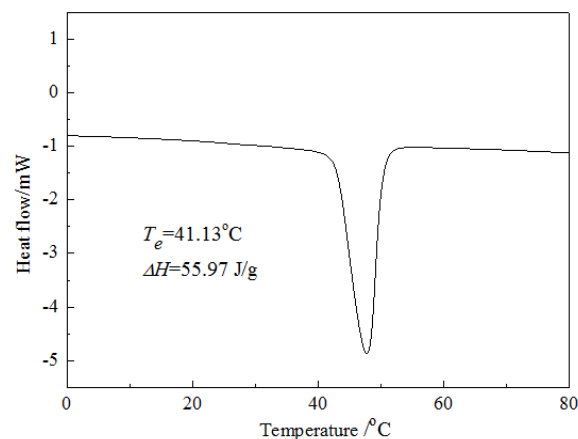


**Figure 4.** DSC Curve of NPG/EP Composite PCM after 100 Times Thermal Cycling Test

## 4. Conclusions

The NPG/EP composite PCM in which NPG working as phase change core and E type epoxy resin as encapsulated matrix was successfully prepared through the melt blending method. The NPG/EP composite PCM was characterized by SEM and FT-IR spectroscopy techniques. It is indicated that by curing and molding with EP simultaneously, NPG has been encapsulated into EP well. There were no chemical reactions between NPG and EP. According to the DSC test results, phase change temperature of the NPG/EP composite PCM was 41.26°C which was similar to that of pure NPG. The latent heat was 57.04 J/g, about 49.6% of the pure NPG. Heating experiment on the composite PCM indicated that EP played an important role in inhibiting the volatilization of NPG in the composite. The volatilization weight loss of the NPG/EP composite PCM rate decreased significantly than that of pure NPG. Furthermore, thermal cycling test confirmed the thermal stability and reliability of the NPG/EP composite PCM. The change on phase change temperature and latent heat of the composite PCM after 100 times heating -cooling thermal cycling was so small that can be neglected in the thermal storage applications.

Based on all results, it can be concluded that the NPG/EP composite PCM can be used in the building energy conservation and solar energy utilization etc. as thermal energy material due to absorption of heat in conjunction of solid-solid phase change of PCM.

## 5. Acknowledgement

## 6. References

[1]   Tyagi Vineet Veer and Buddhi D, " A review on phase change energy storage: materials and applications," Energy Conversiton and Management, vol. 45, Jun. 2004, pp. 1597-1615, doi:10.1016/j.enconman.2003. 09.015.

[2]     N.Soares, J.J. Costa, A.R. Gaspar and P. Santos, "Review of passive PCM latent heat thermal energy storage systems towards buildings' energy efficiency," Energy and Buildings,  vol. 59, Apr. 2013, pp. 82-103, doi:10.1016/j.enbuild.2012.12.042.

[3]     I. S. Jacobs and C. P. Bean, "Thermal and flow behaviors in heat transportation container using phase change material," Energy Conversiton and Management, vol. 49, Apr. 2003, pp. 698-706, doi:10.1016/j.enconman.2007.07.022.

[4]     M. Li and Z. S. Wu, "A review of intercalation composite phase change material: Preparation, structure and properties," Renewable and Sustainable Energy Reviews, vol. 12, May 2012, pp. 2094-2101, doi.org/10.1016/j.rser.2012.01.016.

[5]      D. Meng and L.J. Wang. "Characterization and thermal conductivity of modified graphite/fatty acid eutectic/PMMA shape-stabilized phase change material," Journal of Wuhan University of Technology, vol. 28, Jun. 2013, pp. 586-591, doi:10.1007/s11595-013-0735-0.

[6]     T. Khadiran, M. Z. Hussein, Z. Zaina and R. Rusli, "Encapsulation techniques for organic phase change materials as thermal energy storage medium: A review," Solar Energy Materials & Solar Cells, vol. 143, Dec. 2015, pp. 78-98, doi:10.1016/j.solmat. 2015.06.039.

[7]     X.W. Wang, E.R. Lu, W.X Lin and C.Z. Wang, "Micromechanism of heat storage in a binary system of two kinds of polyalcohols as a solid-solid phase change material," Energy Conversion and Management.vol. 41, Jan. 2000, pp. 135-144, doi:10.1016/S0196-8904(99)00096-5.

[8]     X. W. Wang, E. R. Lu, W. X. Lin, T. Liu, Z. S. Shi, R. S. Tang and C. Z. Wang, "Heat storage performance of the binary systems neopentyl glycol/pentaerythritol and neopentyl glycol/trihydroxy methyl-aminomethane as solid–solid phase change materials," Energy Conversiton and Management, vol. 41, Jan. 2000, pp. 129-134,  doi:10.1016/S0196-8904(99)00097-7.

[9]     S. Divi, R. Chellappa and D. Chandra, "Heat capacity measurement of organic thermal energy storage materials," J. Chem. Thermodynamics, vol. 38, Mar. 2006, pp. 1312-1326, doi:10.1016 /j.jct.2006.02.005.

[10]    Q. Cao and P. S. Liu, "Hyperbranched polyurethane as novel solid–solid phase change material for thermal energy storage," European Polymer Journal, vol. 42, Jul. 2006, pp. 2931-2939, doi:10.1016/j. eurpolymj.2006.07.020