

Investigation on Thermal Properties Enhancement of PEG/CNT Composites as PCM for Thermal Energy Storage

A. Karami, M. Ebrahimi*

Polymer and Color Eng. Dept., Amirkabir University of Technology, 424 Hafez Ave, Tehran, Iran
ebrahimi@aut.ac.ir

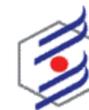
Abstract

Polyethylene glycol (PEG) as a phase change material (PCM) can be used for thermal energy storage (TES). Melting point and phase change enthalpy of this material are in appropriate range; 20.3 °C and approximately 100 J/g, respectively. However, its low thermal conductivity (~ 0.2 W/m.K) limits its application. Therefore, in this project thermal conductivity of PEG was enhanced by utilizing carbon nanotubes (CNT). In order to achieve good compatibility, CNT was first functionalized with surface modification by acid nitric. The modification caused agglomeration which results in improper dispersion. Hence, sonication and planetary ball mill were used for breaking up the agglomerates. The optical microscope (OM) images showed that planetary ball mill was more effective and reduced the cluster size to 2 µm. Then, composites of PEG/CNT were synthesized successfully with CNT loading of 1 and 2 wt.%. Thermal conductivity of the composites were investigated and showed approximately 60% improvement in thermal conductivity of PEG with 2 wt.% CNT. Other thermal properties were studied by differential scanning calorimetry (DSC). The results showed negligible change in phase change enthalpies. Melting and crystallization enthalpy of PEG with 2 wt.% CNT reduced by 1.3 and 5.7%, respectively. It was also observed that the supercooling degree of PEG/CNT composite decreased by 46.20% in comparison to the neat sample. It reveals that CNT also acts as nucleating agent for PEG. Also, specific heat capacities (C_p) of PEG and the composite with 2wt.% CNT versus temperature were calculated from DSC results.

Keywords: PEG, CNT, PCM, thermal energy storage, energy saving, thermal conductivity, latent heat.

Introduction

Nowadays energy management has become an important issue due to limited fossil fuels. Also, greenhouse gas emission from these energy sources has made environmental problems. Therefore, new methods for saving energy has been developed. One of these methods is using phase change materials (PCMs) for thermal energy storage. PCMs are materials that can absorb, store and release large amounts of energy during melting and crystallization processes. This function is done with small volume, efficiently, repeatable and isothermally. Hence, PCMs can be applied in order to stabilize temperature and reduce energy consumption as the result [1–3]. Building industry, electronics, solar energy storage, smart textiles and biomaterials are some fields of application for PCMs [2]. Phase change materials should have appropriate properties. Suitable melting point, high thermal conductivity, large latent heat,



chemical stability, being non-corrosive and non-flammable are some desirable properties for PCMs. Another important parameter of PCMs as storing materials is their specific heat capacity (C_p). High heat capacity enables high heat storage by small volume of material. Furthermore, no supercooling or negligible supercooling degree is an important characteristic of PCMs. Supercooling is defined as difference between melting point and crystallization point which causes extra time for crystallization process [4, 5].

PCMs are mainly classified into two types including organic and inorganic materials. Inorganic PCMs have high thermal conductivity and large latent heat. However, excessive supercooling, irreversible cycles and phase segregation are the main drawbacks of inorganic PCMs. While organic phase change materials are stable, non-corrosive without phase segregation and with negligible supercooling. So, organic PCMs show better properties in comparison with inorganic PCMs [5, 6]. Organic PCMs in spite of many advantages over inorganic PCMs, have weakness of low thermal conductivity. Organic PCMs contain low-molecular weight compounds and polymers. The low-molecular weight type such as paraffins and fatty acids have high vapor pressure which results in explosion danger. Whereas, polymeric PCMs do not have this problem. Polyethylene glycol (PEG) is a polymeric PCM with relatively high latent heat (approximately 100 J/g) and is available in wide range of phase change temperatures from -50 to +100 °C [6, 7].

The main disadvantage of PEG as an organic PCM is its low thermal conductivity which results in reduced heat transfer rate. The thermal conductivity can be enhanced by adding high thermal conductive fillers to PEG. One of the important drawbacks of adding fillers that should be noted is reducing phase change enthalpy since this property originated from PCM [8]. The conductive fillers can be carbon-based materials or metal fillers. Carbon-based materials are chemically inert with high thermal conductivity, low density, high surface area and high porosity. Therefore, these fillers are extensively used. Carbon nanotubes (CNT) is a typical carbon-based material with ultra-high thermal conductivity of 2000-6000 W/m.K and high aspect ratio [7, 9]. In a research Wang et al. reported thermal conductivity enhancement by adding 2 wt.% multiwall carbon nanotubes (MWCNT) to paraffin as the phase change material. It was reported that the thermal conductivity of the composite increased by 35% and 40% in solid state and liquid state, respectively. Also, adding MWCNT led to 1% decrease in latent heat of paraffin [10].

In the present work, PEG was selected as the phase change material and its thermal conductivity was enhanced by using MWCNT. The composites with 1 and 2 wt.% of MWCNT were prepared and characterized.

Experimental

Materials

Polyethylene glycol with molecular mass of 600 g/mol (PEG600) was used as PCM. PEG is an organic material with density of 1.12 g/cm³. The melting point of this material is 20.3 °C and its crystallization point is 8.9 °C. So, the supercooling degree of PEG is 11.4 °C. The phase change enthalpies of PEG are relatively high (102.95 and 106.12 J/g for melting and crystallization processes, respectively). Thermal conductivity coefficients (k) of PEG is in the range of 0.190-0.239 W/m.K at 25-45 °C.

For improving thermal properties of PEG such as increasing thermal conductivity and decreasing supercooling degree, multiwall carbon nanotubes (MWCNT-NC7000) were used. Table 1 shows the properties of MWCNT. Surface modification of CNT was done by using nitric acid. Modification was carried out for better compatibility between CNT and PEG.

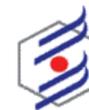


Table 1. properties of MWCNT

Property	Value
Average diameter (nm)	9.5
Average length (μm)	1.5
Surface area (m^2/g)	250

Preparation

First, the surface of CNT was modified by using nitric acid by a reflux system (ratio of nitric acid to CNT was 300:1). The mixture was stirred for 24 hr at 95 °C. Then it was added to deionized water and was filtered. Afterward, it was dried in oven at 65 °C for 24 hr. The modification process caused agglomeration. In order to reduce particle size, CNT was added to water and de-agglomerated with two different methods. In the first method, CNT was ultrasonicated with HIELSCHER ultrasound for 15 min with 200 W power. In the second method, a RETSCH planetary ball mill was used. A LEICA optical microscope (OM) images revealed that planetary ball mill was more effective in reducing the particle size of modified CNT. Hence, this sample was used in the next step.

The modified CNT was mixed with PEG and the mixture was ultrasonicated for 30 min. At last, the water in mixture was eliminated by heating and the composites of PEG/CNT with 1 and 2 wt.% loading of CNT were obtained.

Characterization

The thermal conductivity coefficients of synthesized composites were investigated by DECAGON KD2 pro thermal properties analyzer at 25, 35 and 45 °C. Each measurement was done three times and the mean values were reported. Moreover, other thermal properties (melting and crystallization temperatures and enthalpies) were studied by METTLER differential scanning calorimetry (DSC) with the rate of 5°C/min from -40°C to +40°C under nitrogen atmosphere. Specific heat capacity was also calculated from DSC results.

Results and discussion

CNT modification

In order to compare two methods for de-agglomeration the modified CNT, optical microscopy was used. Fig. 1 shows the OM images of these two methods. As it can be seen, particle size by ultrasonication was reduced to 50 μm . whereas, planetary ball mill reduced the particle size of modified CNT to less than 20 μm . It reveals that planetary ball mill was more effective.

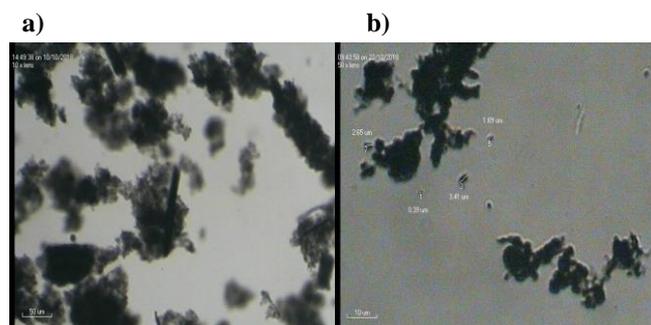


Fig 1. OM images of modified CNT by a) ultrasonication and b) planetary ball mill
Thermal conductivity improvement

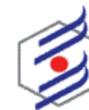


Fig. 2 shows the thermal conductivity coefficients (k) of pure PEG and the composites of PEG/CNT with 1 and 2 wt.% CNT at 25, 35 and 45 °C. The results are also summarized in Table 2. The best result was achieved by PEG with 2 wt.% CNT at 35 °C which shows an important impact on thermal conductivity enhancement of PEG (60.5% enhancement).

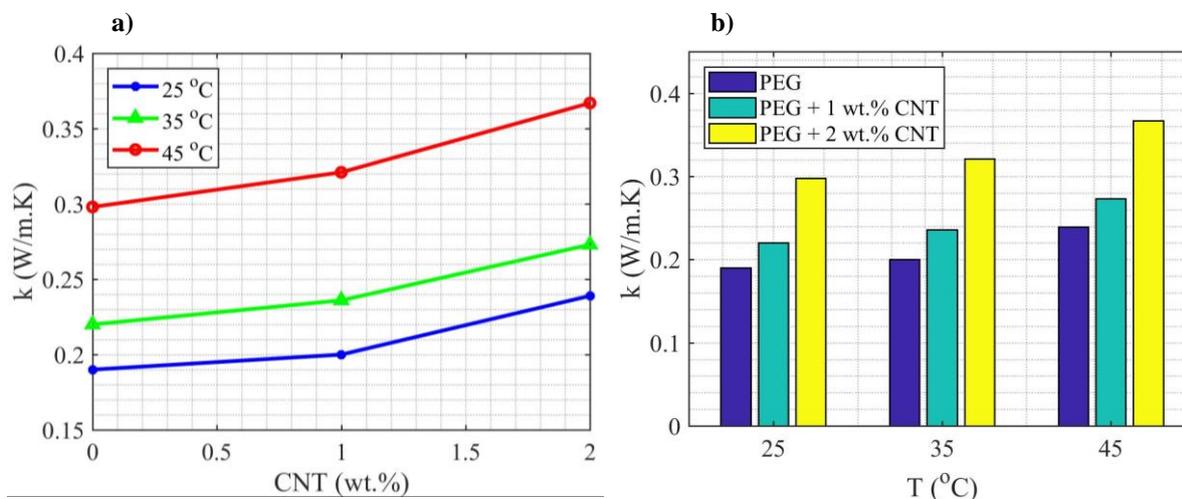


Fig 2. Thermal conductivity coefficients of composites a) vs. CNT content at different temperatures and b) vs. temperature with different CNT contents

Table 2. Thermal conductivity and enhancement at different temperatures

Thermal properties	CNT mass fraction (wt.%)		
	0	1	2
Thermal conductivity at 25 °C (W/m.K)	0.190	0.220	0.298
Thermal conductivity at 35 °C (W/m.K)	0.200	0.236	0.321
Thermal conductivity at 45 °C (W/m.K)	0.239	0.273	0.367
Enhancement at 25 °C (%)	-	15.8	56.8
Enhancement at 35 °C (%)	-	18	60.5
Enhancement at 45 °C (%)	-	14.2	53.5

DSC analysis

Since the composite with 2 wt.% CNT had the best performance for thermal conductivity, this sample was used for DSC analysis in comparison with pure PEG. The DSC curves are shown in Fig. 3 (T_s stands for temperature of the sample). As it can be seen there are two peaks in crystallization process of PEG that can be related to different crystals in PEG. Whereas, by adding CNT the peaks overlapped and a broad peak was formed which shows synchronous formation of crystals by adding CNT. It seems that CNT acted as nucleating agent for PEG. Also, the melting process peak became wide by adding CNT. The detailed results are listed in Table 3. Supercooling degree of PEG was reduced from 11.32 to 6.09 °C (46.20% reduction) by adding CNT which confirms the nucleating agent role of CNT for PEG. It should be noticed that adding CNT did not have significant negative effect on thermal properties of PEG since the melting and crystallization enthalpies decreased only by 1.31% and 5.71%, respectively.

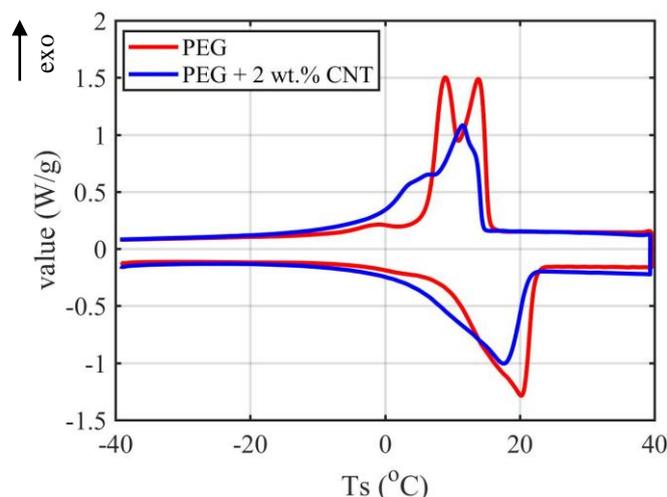
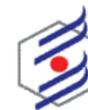


Fig 3. DSC curves of PEG and composite of PEG with 2 wt.% CNT

Table 3. DSC analysis

DSC analysis	Sample	
	PEG	PEG + 2 wt.% CNT
Melting temp. (°C)	20.26	17.67
Melting enthalpy (J/g)	102.95	101.60
Crystallization temp. (°C)	8.94	11.58
Crystallization enthalpy (J/g)	106.12	100.06
Supercooling degree (°C)	11.32	6.09
Melting enthalpy reduction (%)	-	1.31
Crystallization enthalpy reduction (%)	-	5.71
Supercooling degree reduction (%)	-	46.20

Specific heat capacity

The heat capacities of PEG and the composite of PEG with 2wt.% CNT as a function of temperature at constant pressure for heating and cooling processes were calculated from DSC results (Fig. 4). It showed that C_p at phase change temperatures was decreased. While, the mean value of C_p was improved for solid and liquid phases by approximately 20%.

Conclusions

The preparation and thermal properties investigation of PEG/CNT composites for thermal energy storage application were presented. Thermal conductivity of PEG was improved by approximately 60% by adding 2 wt.% CNT. While, the phase change enthalpies did not have considerable change. The other important impact of adding CNT was the reduction of supercooling degree by nucleating mechanism. Specific heat capacity was also improved at solid and liquid phases. The results proved that the PEG/CNT composites are useful for thermal energy storage.

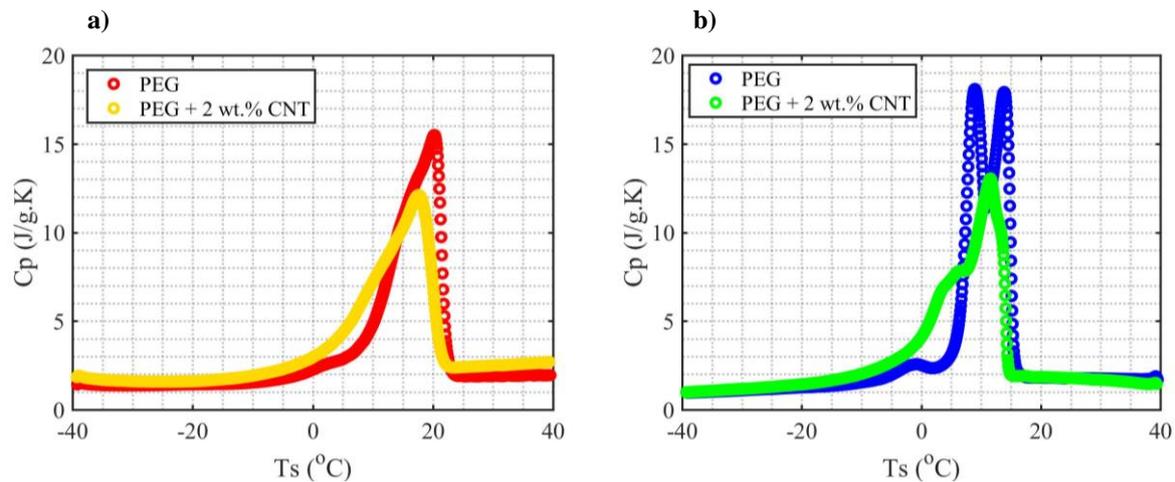


Fig 4. Specific heat capacities of PEG and composite of PEG with 2 wt.% CNT at constant pressure vs. temperature at a) heating process and b) cooling process

References

- [1] Zhang, P., Xiao, X. and Ma, Z. W. , " A review of the composite phase change materials: Fabrication, characterization, mathematical modeling and application to performance enhancement", *Appl. Energy*, 165, 472–510 (2016).
- [2] Pielichowska, K. and Pielichowski, K. , " Phase change materials for thermal energy storage", *Prog. Mater. Sci.*, 65, 67–123 (2014).
- [3] Karaipekli, A., Biçer, A., Sarı, A. and Veer, V. , " Thermal characteristics of expanded perlite /paraffin composite phase change material with enhanced thermal conductivity using carbon nanotubes", *Energy Convers. Manag.*, 134, 373–381 (2017).
- [4] Chieruzzi, M., Cerritelli, G. F., Miliozzi, A. and Kenny, J. M. , " Effect of nanoparticles on heat capacity of nanofluids based on molten salts as PCM for thermal energy storage", *Nanoscale Res. Lett.*, 8, 1–9 (2013).
- [5] Waqas, A. and Ud Din, Z. , " Phase change material (PCM) storage for free cooling of buildings - A review", *Renew. Sustain. Energy Rev.*, 18, 607–625 (2013).
- [6] Li, H., Jiang, M., Li, Q., Li, D., Chen, Z., Hu, W., Huang, J., Xu, X., Dong, L., Xie, H. and Xiong, C. , " Aqueous preparation of polyethylene glycol/sulfonated graphene phase change composite with enhanced thermal performance", *Energy Convers. Manag.*, 75, 482–487, (2013).
- [7] Sarı, A., Bicer, A., Al-Sulaiman, F. A., Karaipekli, A. and Tyagi, V. V. , " Diatomite/CNTs/PEG composite PCMs with shape-stabilized and improved thermal conductivity: Preparation and thermal energy storage properties", *Energy Build.*, 164, 166–175 (2018).
- [8] Qi, G. Q., Yang, J., Bao, R. Y., Liu, Z. Y., Yang, W., Xie, B. H. and Yang, M. B. , " Enhanced comprehensive performance of polyethylene glycol based phase change material



with hybrid graphene nanomaterials for thermal energy storage", *Carbon*, 88, 196–205 (2015).

[9] Sun, Q., Zhang, N., Zhang, H., Yu, X., Ding, Y. and Yuan, Y. , " Functional phase change composites with highly efficient electrical to thermal energy conversion", *Renew. Energy*, 145, 2629–2636 (2020).

[10] Wang, J., Xie, H. and Xin, Z. , " Thermal properties of paraffin based composites containing multi-walled carbon nanotubes", *Thermochim. Acta*, 488, 39–42 (2009).