

NANOCOMPOSITE SANDWICHES CONTAINING PHASE CHANGE MATERIALS

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Abstract: Energy storage has become an important part of renewable energy technology systems. The latent heat energy storage realized using a phase change material (PCM) is one of the most effective techniques of energy storage because of high energy storage density. PCM must be protected with suitable structures against water and other factors. Typical example of it is the encapsulation of PCMs into polymeric capsules. In this study, nanocomposite sandwiches composed from nanofibrous layers containing phase change materials and protective layers were evaluated. In comparison with nonporous polymeric active layers, the nanofibrous PCM rich layer have a higher capability to stabilize and separate PCM.

Keywords: phase change materials, PCM, energy storage, thermal, DSC, contact angle.

1 INTRODUCTION

Phase change capability of water is one of the main factors protecting life in our planet. Without high melting heat and high thermal capacity of water, our climate will be much more extreme. Similar effects are used by many research teams to increase comfort of clothing or protect human body against extreme low or high temperatures. The latent heat energy storage realized using a phase change material (PCM) [1-7] is one of the most effective techniques of energy storage because of their high energy storage density. PCM are capable of storing thermal energy as a result of phase changes (liquid/solid or solid/solid). For our experiment we used PCM materials with high melting heat and optimal melting temperature. Application of PCMs in protected forms is necessary for clothing applications because a liquid form of PCM on textile structures are unstable and will be lost in a short time if it will be not protected. The most common applications of PCM are based on:

- (i) micro-encapsulated form,
- (ii) filling of porous structures as nano-assemblies, foams or aerogels,
- (iii) shape stabilization by forming of polymer blends,
- (iv) creation of nanocomposites with a suitable matrix.

The aim of this contribution is to describe the development of special heat storage sandwiches composed from nanocomposite layer containing PCM and nanofibrous protective layers.

The nanofibrous layer is used as a loaded layer and as a barrier layer to avoid a leakage of molten PCM. These structures can be improved by addition of special components enhancing thermal conductivity and improving electromagnetic shielding. With this improvement, these composite structures can be used for development of special pockets or covers for portable electronic devices such as laptops, smartphones etc., protecting them against sudden heat shocks and avoiding identification of their presence inside.

2 THEORY OF PHASE CHANGE MATERIALS

PCM functionality is based on the heat absorption or release when they undergo a phase change from solid to liquid and vice versa (Figure 1).

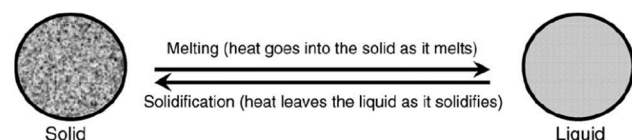


Figure 1 Phase change in PCM

In literature, we can find a large number of phase change materials that are organic, inorganic and eutectic which are active in different temperature ranges. The well-known organic PCMs, with solid-liquid phase transition, are paraffin waxes, poly(ethylene glycol)s, fatty acids and their derivatives. Some organic PCM, such as

polyalcohols and polyethylenes undergo the solid-solid phase transition at a fixed temperature. PEGs as PCMs are very good candidates for filling of porous structures. PEGs are linear dimethyl ether chains with hydroxyl ending groups, HO-CH₂-(CH₂-O-CH₂)_n-CH₂-OH, soluble in water and selected organic solvents. PEGs have relatively large heat of fusion, resistance to corrosion and wide melting point range adjustable by their molecular mass M_w (Table 1) [8-10].

Table 1 Characteristic of PEGs

M_w [g mol ⁻¹]	T_M [°C]	ΔH_{fus} [J.g ⁻¹]	ΔH_{cr} [J.g ⁻¹]
600	22.2	108.4	116
1000	32.0	149.5	140
1500	46.5	176.3	169

Tuning of melting point is simply made by mixing of PEGs with different molecular mass. PEGs are used as PCMs in a variety of thermal storage applications ranging from building envelopes, coated fabrics, foams and fibers. They have a high heat of fusion, low and moderate melting temperature intervals, low vapor pressure, high chemical and thermal stability, non-flammability, biodegradability, non-toxicity, and non-corrosive properties [11, 12, 3, 4]. The melting temperatures T_M , heats of fusion ΔH_{fus} and heats of crystallization ΔH_{cr} of PEGs increase gradually with their molecular mass increase.

3 MATERIALS AND METHODS

A "smart heat storage" nano composite structure was created from a central "active layer" containing a PCM, which was covered by "protective layers" on both sides. The "active layer" and the both "protective layers" contain a nanofibrous layer. As the core of "active layer", the polyamide nanofibrous layer with a fiber diameter approximately 200 nm in a standard planar form was used (Figure 2). The "active layer" was created by loading of the electrospun nanofibrous assembly (10 wt.%) by 90 wt.% of PEG $M_w = 1500$ (melting temperature $T_M = 43-46^\circ\text{C}$).

This "active layer" was covered by "protective layers". Material of the "protective layers" was selected from comparison of 10 types of nanofibrous layers such as PA, PUR and AC, with a different chemical composition and modified by different hydrophobization methods such as plasma deposition, hydrophobic finishes and oleophobic finishes. Criterion of the selection was a repellency of the melted PEG estimated by a modified method of a contact angle measurement. The melted PEG at 70°C was deposited on the tested sample in form of droplet with volume approximately 20 microliters. Droplet was held on the tested sample for 10 minutes at 70°C. The sample was then cooled at standard laboratory conditions for 2 hours and the contact angle was estimated by the optical method

with the image analysis system. For the prepared samples, the heat of fusion was evaluated using DSC measurements.

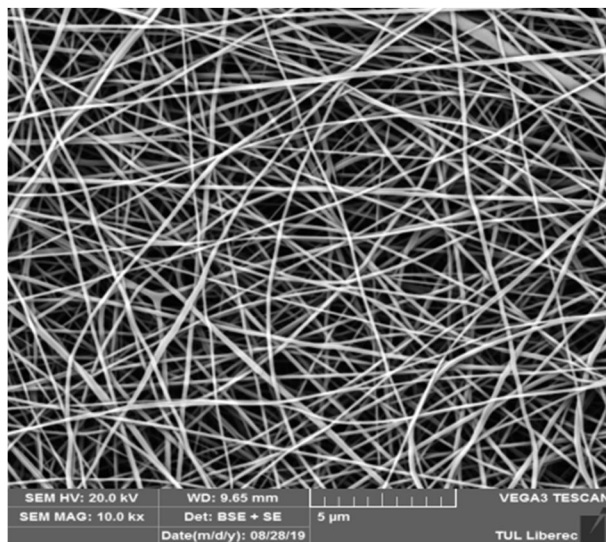


Figure 2 Polyamide nanofibrous layer used as active layer containing PCM

3.1 Thermal effect calculation

The heat evolved by the phase change is equal to:

$$Q = m L = V \rho L \quad (1)$$

where: m is mass, V is volume and L [J/g] is latent heat (e.g. for PEG it is 121).

The heat produced by heating (sensible heat storage) is equal to:

$$Q = m c dT = V \rho c dT \quad (2)$$

where: dT is temperature change and c [J/(kg.K)] is specific heat (for water it is 4190).

The heat transferred by conduction is equal to:

$$\frac{Q}{t} = \lambda A \frac{dT}{h} \quad (3)$$

where: λ [W/(m.K)] is thermal conductivity (air 0.026, water 0.68, skin 0.09, PES 0.2, Ag 428), A is cross section area, t is time and h is thickness.

Let PCM materials of mass m [kg] having heat of fusion per unit mass ΔH_{fus} [J/kg], average specific heat between initial temperature T_i [°C] and melting temperature T_M [°C] is C_{sp} [kJ.kg⁻¹.K⁻¹] and average specific heat between T_M and final temperature T_f [°C] is equal to C_{fp} [kJ.kg⁻¹.K⁻¹]. The total stored heat Q [J] depends on the final temperature and its relation to initial and melting temperature.

$$Q = m \left[C_{sp} (T_M - T_i) + f (\Delta H_{fus} + C_{sp} (T_f - T_M)) \right] \quad (4)$$

where: f is fraction of melted PCM.

3.2 Layer containing PCM

Let us assume a layer containing PCM with volume ratio v_{PCM} , density ρ_{PCM} , latent heat of phase change L . Fibrous layer with length l_F and width c_F , i.e. surface area $S_F = l_F \cdot c_F$ and thickness h composed from fibers with density ρ_F . Planar mass:

$$w_T = m_T / S_F = \rho_T h \quad (5)$$

($gsm/1000$, where gsm is weight of fabric in grams per surface in meter squared). Total mass of fibrous layer m_T is equal to:

$$m_T = \rho_T V_T = \rho_T S_F h = (1 - P_0) h \rho_F S_F \quad (6)$$

Mass of PCM m_{PCM} is equal to:

$$\begin{aligned} m_{PCM} &= \rho_{PCM} v_{PCM} V_T = \frac{\rho_{PCM} v_{PCM} m_T}{\rho_T} \\ &= \frac{\rho_{PCM} v_{PCM} m_T}{\rho_{PCM} v_{PCM} + \rho_F (1 - v_{PCM})} = \rho_{PCM} v_{PCM} h S_F \end{aligned} \quad (7)$$

Heat due to phase change Q_{PCM} is then equal to:

$$\begin{aligned} Q_{PCM} &= m_{PCM} L = \frac{\rho_{PCM} v_{PCM} m_T L}{\rho_{PCM} v_{PCM} + \rho_F (1 - v_{PCM})} \\ &= \rho_{PCM} v_{PCM} h S_F L \end{aligned} \quad (8)$$

For the case of heat transfer in PCM of volume fraction v_{PCM} from solid to liquid phase, when convection is governing process, is time to phase change equal to:

$$t[s] = \frac{h^2 v_{PCM} \rho_{PCM} L}{\lambda dT} \quad (9)$$

4 RESULTS AND DISCUSSION

The specified thermal phenomena of PCM can be characterized by using differential scanning calorimetry (DSC), determining the relevant equilibrium regions, phase transitions and related temperatures. The modulation of the thermal signal provides information about the phase transition and compositional homogeneity. The DSC trace of smart heat storage" sandwiches is shown in Figure 3. The heat of fusion 148 J/g of the three-layer composite structure was obtained as area under solid line peak on DSC trace (Figure 3).

The contact angle measurement by using of PEG droplets was complicated by spontaneous crystallization of melted PEG. In addition, there appeared higher lateral adhesion forces typical for hydrophobic surfaces [13]. Resulted droplets are then significantly asymmetric (Figure 4).

Measurement of contact angle between PEG and the nanofibrous layer showed high attraction forces between melted PEG and the nanofibrous layer. Among all the protective nanofibrous layers tested, only polyamide 6 (PA) nanofibrous layer modified by polytetrafluoroethylene (PTFE) was found effective with an estimated average contact angle

between nanofibrous mat and PEG solid droplet approximately 120° (Figure 5). The "protective layers" were then in final form realized by PA nanofibrous assembly prepared by electrospinning and modified by PTFE.

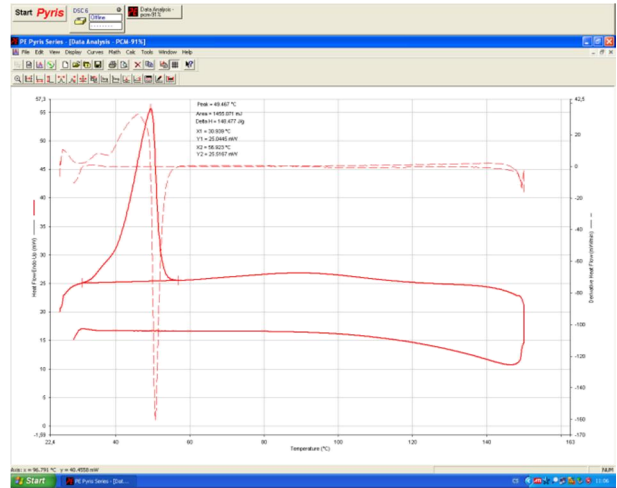


Figure 3 DSC trace of smart heat storage sandwiches



Figure 4 Deformation of PEG solid droplets on nanofibrous layer

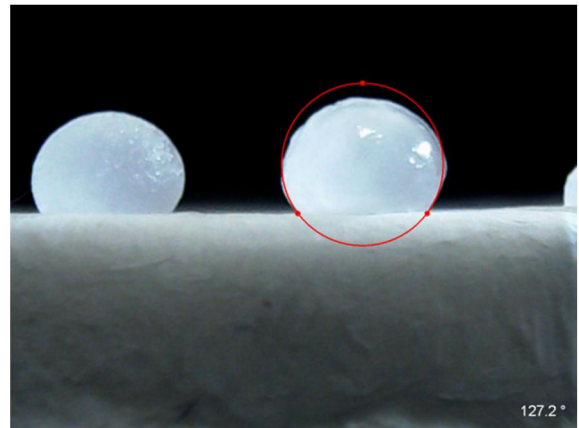


Figure 5 Contact angle measurement - PEG solid droplets on nanofibrous layer

The "active layer" containing PEG was combined with the "protective layers" (Figure 6) to build up the "smart heat storage" sandwiches.

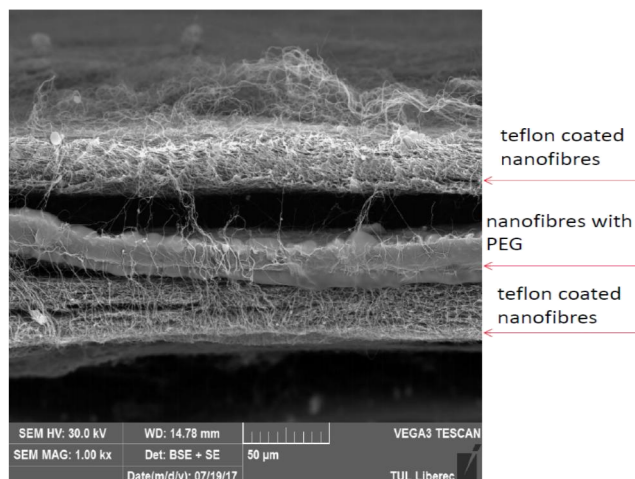


Figure 6 "Smart heat storage,, sandwiches

The protective layers protect PEG leakage present in the "active layer" not only during heat exposition, but also during washing process or during ironing process.

This "smart heat storage" sandwiches are in fact self-stabilized by the behavior of PCM rich active layer and protective layers repellency against molten PEG.

5 CONCLUSIONS

In this study, the "smart heat storage" nanocomposite sandwiches containing PCM were created and tested. The contact angle between melted PEG and the nanofibrous layer showed high attraction forces between both materials avoiding leakage. Also, the influence of molecular weight on the phase transition characteristics of PEG, determined by DSC, can be considered as an efficient tool for tuning thermal energy storage range. These sandwiches can be used for selected clothing applications due to their extreme heat storage capacity, textile character of surface and water vapor permeability.

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6 REFERENCES

1. Mondal S.: Phase change materials for smart textiles - An overview, *Applied Thermal Engineering* 28(11-12), 2008, pp. 1536-1550, <https://doi.org/10.1016/j.applthermaleng.2007.08.009>
2. Khosrojerdi M., Mortazavi S.M.: Impregnation of a porous material with a PCM on a cotton fabric and the effect of vacuum on thermo-regulating textiles, *Journal of Thermal Analysis and Calorimetry* 114, 2013, pp. 1111-1119, <https://doi.org/10.1007/s10973-013-3144-x>
3. Gines J.M., Arias M.J., Rabasco A.M., Novak C., Ruiz-Conde A., Sanchez-Soto P.J.: Thermal characterization of polyethylene glycols applied in the pharmaceutical technology using differential scanning calorimetry and hot stage microscopy, *Journal of Thermal Analysis* 46, 1996, pp. 291-304, <https://doi.org/10.1007/BF01979969>
4. Constantinescu M., Dumitrache L., Constantinescu D., Anghel E.M., Popa V.T., Stoica A., Olteanu M.: Latent heat nano composite building materials, *European Polymer Journal* 46, 2010, pp. 2247-2254, <https://doi.org/10.1016/j.eurpolymj.2010.09.007>
5. Bo-an Y., Yi-Lin K., Yi L., Chap-Yung Y., Qing-wen S.: Thermal regulating functional performance of PCM garments, *International Journal of Clothing Science and Technology* 16(1/2), 2004, pp. 84-96, <https://doi.org/10.1108/09556220410520388>
6. Chen C., Wang L., Huang Y.: Electrospun phase change fibers based on polyethylene glycol/cellulose acetate blends, *Applied Energy* 88(9), 2011, pp. 3133-3139, <https://doi.org/10.1016/j.apenergy.2011.02.026>
7. Sharma A., Tyagi V.V., Chen C.R., Buddhi D.: Review on thermal energy storage with phase change materials and applications, *Renewable and Sustainable Energy Reviews* 13(2), 2009, pp. 318-345, <https://doi.org/10.1016/j.rser.2007.10.005>
8. Lane G.A.: *Solar Energy Storage: Latent Heat Materials*, Vol. II, Technology, CRC Press: New York, 1986
9. Han S., Kim Ch., Kwon D.: Thermal degradation of poly(ethyleneglycol), *Polymer Degradation and Stability* 47(2), 1995, pp. 203-208, [https://doi.org/10.1016/0141-3910\(94\)00109-L](https://doi.org/10.1016/0141-3910(94)00109-L)
10. Pielichowski K.: Thermal energy storage systems based on poly(vinyl chloride) blends, *European Polymer Journal* 35(1), 1999, pp. 27-34, [https://doi.org/10.1016/S0014-3057\(98\)00107-4](https://doi.org/10.1016/S0014-3057(98)00107-4)
11. Craig D.Q.M., Newton J.M.: Characterization of polyethylene glycols using differential scanning calorimetry, *International Journal of Pharmaceutics* 74(1), 1991, pp. 33-41, [https://doi.org/10.1016/0378-5173\(91\)90405-D](https://doi.org/10.1016/0378-5173(91)90405-D)
12. Sarier N., Onder E.: Thermal insulation capability of PEG-containing polyurethane foams, *Thermochimica Acta* 475(1-2), 2008, pp. 15-21, <https://doi.org/10.1016/j.tca.2008.06.006>
13. McHale G., Shirtcliffe N.J., Newton M.I.: Contact-angle hysteresis on super-hydrophobic surfaces, *Langmuir* 20(23), 2004, pp. 10146-10149, <https://doi.org/10.1021/la0486584>