

# Study of thermo-physical properties and cycling stability of D-Mannitol-copper oxide nanocomposites as phase change materials



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## ARTICLE INFO

### Article history:

Received 20 January 2017  
Received in revised form 4 October 2017  
Accepted 18 October 2017  
Available online xxx

### Keyword:

D-Mannitol  
Phase change materials  
Nanoparticles  
Thermal energy storage system  
Latent heat of fusion  
Latent heat of solidification  
Melting point and solidification point

## ABSTRACT

Sugar alcohols (SA) are emerging as one of better energy storage materials for thermal energy storage (TES) application due to its phase change temperature ranges ( $-15$  to  $245$  °C) and considerable phase change enthalpies of  $100$ – $430$  kJ/kg. However, the main challenges include the low thermal response of the phase change materials (PCM) owing to its very low thermal conductivity values. In this study, D-Mannitol (DM)-copper oxide (CuO) nanocomposites (DM-CuON) were prepared using dispersion technique to form high thermal conductive nanocomposites. In this view, copper oxide (CuO) nanoparticles were mixed in DM in various mass fraction of  $0.1$ ,  $0.2$  and  $0.5$  wt.% using high-speed ball mill. Structural analysis was done by SEM and crystallography by XRD diffraction techniques. The XRD data reveal that the pure DM exhibited the polymorphic form of beta ( $\beta$ ) phase. By varying the weight percentage from  $0.1$  to  $0.5$  wt.% the rate of relative crystallization increased as compared to pure DM. Thermal conductivity enhancement of  $25.2\%$  was observed for DM-CuON with  $0.5$  wt.%. It was observed that the interaction between CuO nanoparticles and DM were only physical in nature which confirmed its high chemical stability. After repeated heating/cooling cycles the heat of fusion decreased yet it showed high latent heat value of  $256.20$  kJ/kg,  $252.48$  kJ/kg,  $246.85$  kJ/kg and  $240.78$  kJ/kg after 50 cycles and  $241.16$  kJ/kg,  $237.49$  kJ/kg,  $229.86$  kJ/kg and  $205.48$  kJ/kg after 100 cycles for DM and DM-CuON. Mass changes observed were less than  $3\%$  after thermal cycling for a temperature range up to  $250$  °C. Overall CuO helps to achieve improved thermo-physical and heat storage characteristics for DM-CuON which suggest their potential candidate of usage in the medium temperature thermal energy storage system.

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## 1. Introduction

A lot of research interest is shown in latent heat energy storage (LHES) system which can reduce the gap between energy production and energy consumption [1]. A practical LHES mainly consists of heat storage material known as phase change materials (PCM). These phase change materials undergo phase change at nearly constant temperature conditions with the high amount of thermal energy that can either be stored or released in the form of latent heat. Energy is stored in the form of sensible heat, latent heat and thermochemical heat storage [2]. Phase change materials can be classified into organic, inorganic and eutectics. The major disadvantages of PCM were found to be its very low thermal conductivity which decreases its energy storage and discharging rates [3]. To address this issue many authors have researched

methods to increase its thermal conductivity of PCM. One of the best methods to address the issue is to form a nanocomposite PCM with nanoscale fillers, which has received a substantial attention from the research community. The nanofillers consist of metal/metal oxide nanoparticles, metal nanowires carbon nanofibers, carbon nanotubes and graphene/graphene nanoplatelets. Although a very little work has been presented for the effect on thermophysical properties of sugar alcohols after the addition of nanoparticles. The main requirement of PCM is its long-term stability after its repeated melting and freezing cycling. This stability includes thermal, chemical and physical properties [4]. Sugar alcohols can be a suitable phase change materials due to its high phase change enthalpies and its range of melting points. Until recently very less research has been done on the application of sugar alcohols as heat storage materials for LHES. Three different type of modification of D-Mannitol were studied by Burger et al. [5]. Three crystal forms were investigated and each of the thermo-physical, crystallographic and optical characterization was done. DSC, FTIR, FT-Raman, Thermo-microscopy and powder compaction studies were performed to characterize the samples. Pitkanen et al.

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### Nomenclature

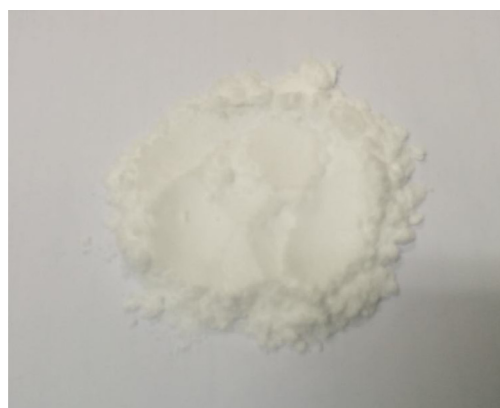
#### Abbreviation

|           |   |
|-----------|---|
| CuO       | Copper oxide nanoparticle                       |
| DM        | D-Mannitol                                      |
| DM + CuON | D-Mannitol-copper oxide nanocomposite           |
| DLS       | Dynamic light scattering                        |
| DSC       | Differential scanning calorimetry               |
| FT-IR     | Fourier transform infra-red                     |
| FWHM      | Full width half maximum                         |
| JCPDS     | Joint committee on powder diffraction standards |
| LHES      | Latent heat energy storage                      |
| NePCM     | Nano enhanced phase change material             |
| PCM       | Phase change material                           |
| SA        | Sugar alcohol                                   |
| SEM       | Scanning electron microscopy                    |
| TGA       | Thermogravimetric analysis                      |
| TES       | Thermal energy storage                          |
| XRD       | X-ray diffraction                               |

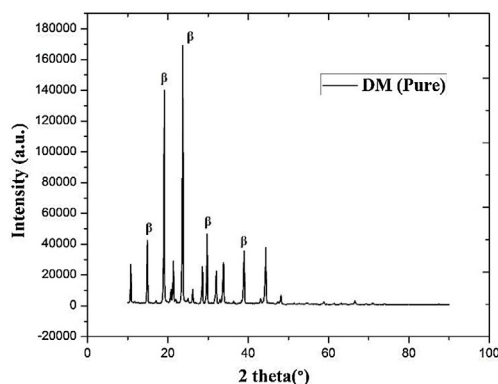
#### Greek Symbol

$\beta$  Beta

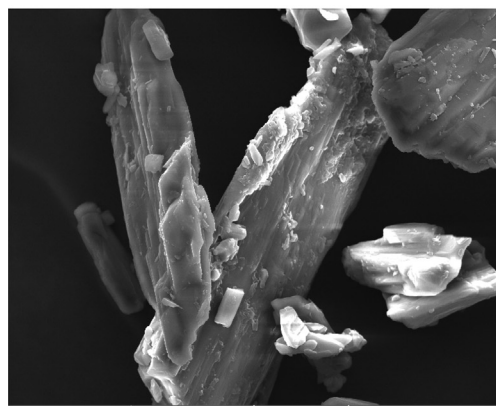
[6] studied the behavior of D-Mannitol using X-ray diffraction analysis. The crystallization of D-mannitol from the melt gave seven peaks in the DSC between 95 and 126 °C depending on cooling rates and the amounts of sample. Gil et al. [7] investigated the thermal behavior of D-Mannitol when used in thermal energy storage unit. They found that for two different experimental conditions (A, B) with different cooling rates, the melting temperature was different. For experimental A with cooling rate of 0.17 °C/min, the melting temperature was between 160 °C and 170 °C. For experiment B with cooling rate of 0.36 °C/min, the melting rate was between 150 °C and 162 °C. They concluded that D-Mannitol is one of the potential candidates to be used in LHES due to its high latent heats. Sole et al. [8] studied the stability of sugar alcohols (D-Mannitol, *myo*-inositol and Galactitol) as PCM for thermal energy storage. The cycling stability was studied by DSC and the chemical stability with FT-IR. The influence of oxygen instability and the temperature range effect was also presented. Kumaresan et al. [9] studied the thermo-physical properties of D-Mannitol. The results showed that due to the high latent heat capacity of the PCM and a large temperature difference of 132 °C between the melting point and decomposition temperature make D-Mannitol as good phase change materials for latent heat storage in medium temperature applications. Paul et al. [10] investigated the thermo-physical properties of Galactitol and Mannitol as a eutectic mixture for latent heat storage system. The eutectic mixture was obtained at 30:70 molar ratio of Galactitol and Mannitol and the melting point and latent heat of fusion of the



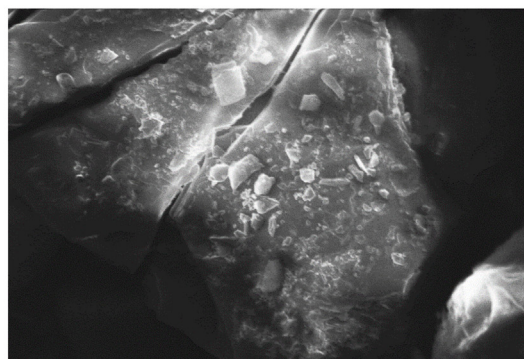
(a)



(b)



(c)



(d)

Fig. 1. (a) Powder samples of pure DM (b) XRD spectra of pure DM (c) SEM image of DM at magnification of 800 $\times$  (d) SEM image of DM at magnification of 5000 $\times$ .

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