



Crystallization of inorganic salt hydrates in polymeric foam for thermal energy storage application



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ABSTRACT

Inorganic salt hydrates as phase change material (PCM) offers high energy storage density, low heat of combustion and relatively high thermal conductivity than organic PCMs at a reasonable cost. Moreover, these are nonflammable and also available in the large temperature range for the thermal energy storage (TES) application. However, phase segregation, supercooling and incongruent melting are the main disadvantages which confine them for TES application. In this present study, open cell polyurethane foam (PU foam) as a heterogeneous surface was introduced to mitigate the problem of phase segregation during its repeated thermal cycles. Composite (PU-PCM) having a combination of porous polyurethane foam sheet and saturated inorganic salt solution, by soaking different saturated salt solutions within pores, was prepared. Solution crystallization process was carried out to develop inorganic salt hydrate crystals within the pores from their aqueous solutions. For thermal insulation application, a model experimental setup was constructed and performance of PU-PCM composite sheet compared with the performance of dry PU foam. Various melting and freezing cycles of salt hydrates inside the porous structure were analyzed and the results are discussed.

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1. Introduction

Non-renewable energy resources such as coal, gas, or oil are depleting with time and in future period these sources will eventually finish. Storage of energy from renewable sources such as wind, solar power etc. is essential for fulfilling our daily energy needs. Conserving energy not only helps to conserve resources but also takes into a reduction of environmental pollution, financial savings.

Latent Heat Storage (LHS) Systems consisting PCM provide high energy storage density per unit mass than other heat storage medium. These PCMs undergo a phase change from solid to liquid or liquid to gas or vice versa, within the temperature range experienced [1]. During environmental temperature fluctuations, when material changes phase from solid to liquid (endothermic reaction), PCM absorbs heat energy in the form of latent heat of fusion. Similarly, upon cooling, PCM desorbs the same amount of energy by changing its phase from liquid to solid (exothermic reaction) [2].

Application of PCMs as latent heat thermal storage systems includes, maintenance of building's cooling and heating needs during off-peak hours, textiles for relief from hot and cold conditions, shipping containers and food products that require maintaining the desired temperature for longer periods, refrigerators and freezers that uses high energy etc. PCMs can be able to fulfill the demand for eco-friendly energy-saving materials. PCMs can be classified as organic (paraffin's, fatty acids), inorganic (salt, metallic and salt hydrates), eutectics (mixtures having a sharp melting point) (Fig. 1). A large number of possible materials and desirable thermo physical, kinetic and chemical properties required for ideal PCM are reported [3–6].

Salt hydrates consists of inorganic salts (AB) and water (H₂O), which form a typical crystalline solid with a general formula (AB·xH₂O). Salt hydrates are the oldest and most studied for their use in latent heat thermal energy storage systems. They can be used alone or as eutectic mixtures. Advantages of salt hydrates includes (i) High latent heat of fusion per unit volume at its melting point (ii) High thermal conductivity (as much as two times compared to paraffin) (iii) Small volume changes during phase change (iv) Large resource available with suitable properties (v) No or limited fire risk, Slightly toxic and Inexpensive [3,5]. List of different salt hydrates used as PCM with their melting point and latent heat of fusion are reported [5,7]. Major problem occurs during their

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Nomenclature

T_1	Temperature at inner chamber of jacketed glass reactor
T_2	Temperature at chiller or outside of jacketed glass reactor
ΔT	Temperature difference ($T_2 - T_1$)
PCM	Phase change material
TES	Thermal energy storage
DSC	Differential scanning calorimetry
PU Foam	Open cell polyurethane foam
PU-N	Composite having Na_2SO_4 salt solution soaked within PU foam
PU-M	Composite having $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ salt solution soaked within PU foam
PU-NM	Composite having mixture of Na_2SO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ salt solution soaked within PU foam
PU-PCM	Composite having a combination of porous polyurethane foam sheet and a PCM within its pores.

application in TES systems includes (i) phase segregation/incongruent melting during repeated thermal cycles (ii) Spontaneous nucleation of undesired lower hydrates (iii) Supercooling due to its weak nucleation property. Various literature has described the solution to above problem for salt hydrates. Some of those includes (i) Adding excess water to completely dissolve the salt [8] (ii) Adding the thickening agents [9] (iii) Mechanical stirring of the mixture [10] (iv) Adding nucleating agents [11] (v) Addition of certain chemicals that prevent the nucleation of lower salt hydrates and also increases the solubility of lower salt hydrates in the solution over original salt hydrate [5] and (vi) Microencapsulation of salt hydrates [12].

Present work deals with an idea that reduces the phase segregation of salt solutions by incorporating them into an open cell polyurethane foam (PU Foam). PU Foam has perfect insulation properties like low thermal conductivity, low density, and superior mechanical properties. PU foam has honeycomb like voids that trap air and offer low thermal conductivity medium. It has been widely used as high performance insulating material for buildings

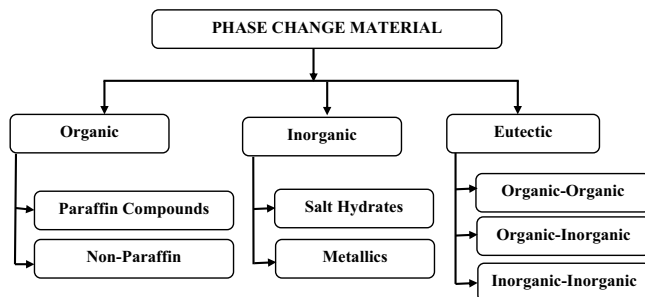


Fig. 1. Classification of Phase Change Materials [5].

Table 1
Polyurethane Composites and their specifications.

Composite Name	Salt Solution Soaked within PU Foam (Concentration)
PU-N	64 gm Na_2SO_4 in 150 ml distilled water (0.3 wt% Na_2SO_4)
PU-M	97 gm $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 120 ml distilled water (0.21 wt% MgSO_4)
PU-NM	64 gm Na_2SO_4 + 64 gm $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 150 ml distilled water (0.23 wt% Na_2SO_4)
Dry PU Foam	No salt solution added

and in some technical applications like heat exchangers, cooling pipes and many more [13].

Studies on PU foam in combination with organic phase change materials (PU-PCM foam) for thermal energy storage and enhancement of thermal insulation capability were reported [14]. PU-PCM foams were prepared by encapsulation [15–17] or direct incorporation [14,18] of PCM into PU foam. Aydin incorporated myristyl myristate with PU foam for thermal energy storage [19].

Comparing PU foam and PU-PCM foam, a PU-PCM with 22.6 wt % PCM, absorbed an excess enthalpy of 45.7J/g which is 34% increase in total heat absorption. Different mass ratios of n-hexadecane and n-octadecane are incorporated into PU-foam by Sarier [14]. Polyethylene glycol (PEG) compounds have the advantages of high heat of fusion, phase change repeatability, chemically stable, non-corrosive and lowcost. PU foam incorporated with three different concentration of PEG enhanced the thermal insulation [20].

In this research work, solution crystallization methodology to produce hydrate salt crystals inside pores of open cell PU foam is studied. Different solutions of salts like Na_2SO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and their mixture were soaked inside the PU foam pores. Then these PU-PCM composite sheets are used to study hydrate phase segregation and energy storage capability. For an observed temperature range, thermal insulation capability were performed and results are discussed.

2. Experimental

2.1. Materials and equipment's used

Sodium sulfate anhydrous (Na_2SO_4) and Magnesium Sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) each having 99% purity was used to prepare aqueous saturated salt solutions. Open cell polyurethane foam sheets of thickness 0.01m, with the density of 32 kg m^{-3} was used as heterogeneous support. Various equipment's used for this experiment are listed below.

- Chiller: MC3i- supplied by IKA® India Private Limited
- Jacketed Glass Reactor: Dimensions: Diameters 0.075 m, 0.1 m and height 0.13 m, 0.15 m for inner and outer jacket respectively
- Hot Plate with Stirrer: Manufactured by REMI Laboratory Instruments, Model no. 2 MLH, having 300 W of heating and two liter stirring capacity
- Vacuum Filtration Unit: Vacuum pump attached with filtration unit was used for separation of undissolved solids from aqueous salt solution.

2.2. Methods and procedures

2.2.1. Preparation of saturated salt solutions and PU-PCM composite

Aqueous saturated solutions were prepared by mixing different weight fractions of salts in distilled water (Table 1). Concentration of these salt solutions were fixed from their binary phase diagram such that they will undergo phase change during experimental

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