



Tuning of thermal properties of sodium acetate trihydrate by blending with polymer and silver nanoparticles

B.M.L. Garay Ramirez^a, Christ Glorieux^b, E. San Martin Martinez^{a,*}, J.J.A. Flores Cuautle^b

^aCentro de Investigación en Ciencia Aplicada y Tecnología Avanzada del Instituto Politécnico Nacional, Legaria 694, Colonia Irrigación, C.P. 11500 México, D.F., Mexico

^bLaboratorium voor Akoestiek en Thermische Fysica (ATF), Dept. Physics and Astronomy, Katholieke Universiteit Leuven, Belgium

HIGHLIGHTS

- The addition of silver nanoparticles reduced the supercooling of PCM.
- Thermal properties of the PCM are improved with a blend of polymers.
- The latent heat recovery of the PCM is higher with silver nanoparticles.
- The combination of Polymers and silver nanoparticles reduces the segregation phase.

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ABSTRACT

The use of phase change materials (PCMs) is one of the pathways for the storage of temporarily excessive energy from natural sources (solar) and industry for use at a more suitable later time. One of the materials with a high energy storage density is sodium acetate trihydrate (SAT), on which several studies were conducted in order to solve phase segregation and supercooling problems, e.g. by adding polymers and nucleating agents. Here we investigate the effectiveness of adding a polymer blend of carboxymethyl cellulose (CMC) and silica gel to avoid phase segregation, and silver nanoparticles (AgNPs) as nucleating agent. The synthesis of silver nanoparticles was carried out by a green method in CMC as a way to ensure compatibility with SAT. The addition of AgNPs in higher concentrations to 0.5% reduces supercooling, and mixing silica gel with CMC to avoid segregation phase, yields an increment in the stability of the phase change behavior, during heating and cooling cycles. The latent heat release upon crystallization of the PCM was optimum for the mixture with 0.5% AgNPs, and for the highest amounts of CMC with respect to silica gel, with nearly 95% of latent heat recovery compared to pure SAT.

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1. Introduction

There is a clear necessity to rationalize the use of energy in modern society. With this goal several areas of knowledge are exploring options to improve energy efficiency through the development of devices and energy storage systems in order to reduce the mismatch between supply and demand [1]. Energy excess not used in processes should be stored for later use [1,2]. One of the pathways for storage is the use of phase change materials (PCM), due to their high density of energy storage as latent heat. A great variety of organic and inorganic materials have been studied and selected according to the kind of energy that needs to be stored and transferred to systems or processes [3]. PCMs are nowadays

present in several areas of application, e.g. for building air conditioning [4–6], electronic cooling [7,8], preservation of food [9,10], solar energy storage [11–13], waste heat recovery [14,15], factories [16] and textiles [17]. The latent heat of PCMs that are based on inorganic salts (250–400 kJ/dm³) is almost double compared to organic ones (128–200 kJ/dm³) [18,19], and they are cheaper and commercially available. However, they have the disadvantage of strong supercooling and they are corrosive in contact with metals [20,21]. Moreover, under continuous cycles of melting and crystallization, due to the large difference in density between water and the components of the hydrated salt, segregation occurs, resulting in poor crystallization and deteriorating thermophysical behavior. In order to prevent phase segregation it has been proposed to modify the PCM composition to push the material from incongruent to congruent behavior, by adding gelling or thickening materials to avoid segregation, and nucleating agents to reduce supercooling [19,22].

* Corresponding author. Tel.: +52 55 57296300x67769; fax: +52 55 55575103.
E-mail address: esanmartin@ipn.mx (E. San Martin Martinez).

Since sodium acetate trihydrate (SAT) is an excellent PCM by virtue of its high energy storage density and thermal conductivity, several investigations were conducted to counter the problems above, mainly by using thickening agents such as cellulose derivatives, silica gel, sepiolite, diatomaceous earth [23], starch (wheat flour), methylhydroxyethyl-cellulose, methylcellulose [20], acrylic acid copolymer, carboxymethyl cellulose (CMC), and polyvinyl alcohol (PVA) [24]. Unfortunately gels formed with polymers are highly viscous and difficult to handle. Blending also lowers the energy storage capacity and increases the melting temperature.

In order to reduce supercooling, various (hydrated salt) nucleating agents have been studied, K_2SO_4 [25], $SrSO_4$, $Na_2P_2O_7 \cdot 10H_2O$ and carbon (1.5–6.7 μm) [24], $NaBr \cdot 2H_2O$ or $NaHCO_3 \cdot 3H_2O$, polyethylene powder [26], $Na_2SO_4 \cdot 10H_2O$, $Na_2CO_3 \cdot 10H_2O$, $Na_4P_2O_7 \cdot 10H_2O$ and $Na_3PO_4 \cdot 12H_2O$ [27], $Na_2HPO_4 \cdot 12H_2O$, $Na_3PO_4 \cdot 12H_2O$, $Na_2CO_3 \cdot 10H_2O$, $Na_2SiO_3 \cdot 9H_2O$ and $Na_2B_4O_7 \cdot 10H_2O$ [28]. Overall these nucleation agents decrease the SAT energy storage capacity, and make it less stable, explaining the significant spread in the results.

Also nanoparticles were considered as candidates for serving as nucleating agent by increasing the surface area. Adding 5 wt% of aluminum nitride (AlN) [29], 5 wt% or 4 wt% Si_3N_4 , 10 wt% ZrB_2 , 2 wt% SiO_2 , BC_4 , SiB_6 has been shown to eliminate the supercooling of SAT [30]. However, the use of high concentrations of nanoparticles is not viable due to the cost of synthesis, problems of homogeneity, and reduction of the heat storage capacity.

In this article we investigate the feasibility of blending small quantities (less than 3%) of (organic) carboxymethyl cellulose (CMC) into SAT to improve its thermal properties, silica gel (inorganic) to limit phase segregation, in combination with Na_2SO_4 and

silver nanoparticles (concentration less than 1%) to trigger nucleation and reduce supercooling. The preparation of the samples is described and their characteristics were determined by UV–vis spectroscopy and Transmission Electron Microscopy (TEM). Their performance as heat storage material was determined by Differential Scanning Calorimetry (DSC) and controlled thermal cycling. Response surface methodology (RSM) is used in order to find the parameters for optimum functionality.

2. Materials and methods

2.1. Materials

For the silver nanoparticle synthesis, silver nitrate ($AgNO_3$, 99.85% Acros Organics), sodium hydroxide (NaOH, 98%), sodium carboxymethyl cellulose (CMC, $\geq 99.5\%$ Sigma–Aldrich), and D-glucose (Bioxtra $\geq 99.5\%$, Sigma–Aldrich) were used. The resulting blend was used to improve the characteristics of Sodium Acetate Trihydrate (SAT, Bio ultra, $\geq 99.5\%$ Sigma–Aldrich) provided the heat storage characteristics. Also anhydrous sodium sulfate (ACS reagent, $\geq 99.0\%$, Sigma–Aldrich) and silica gel powder (J. T. Baker Chemicals) were blended into the PCM.

2.2. Preparation of silver nanoparticles

Aqueous solutions of CMC (0.54% w/v) and D-glucose (0.25 M) were prepared. After complete dissolution in 90 ml of the water, 10 ml aqueous solution of the silver nitrate (0.17 M) was added drop by drop in a three-neck ball glass and further magnetically stirred at 70 °C. In all experiments deionized water was used (18.2 $\mu\Omega/cm$),

Table 1
Response surface design for SAT, polymer blend and AgNPs.

Run	Factor A CMC/gel (%)	Factor B: AgNPs (%)	Onset (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	Supercooling (°C)	Latent heat (%)
1	50.00	0.92	57.8	62.7	235	59.15	0.1	3.55	0.04
2	50.00	0.50	58.7	63.3	242	51.20	213	12.09	87.95
3	50.00	0.50	59.2	63.3	238	41.32	167	21.95	69.93
4	99.50	0.50	59.1	62.2	234	44.66	208	17.59	88.85
5	15.00	0.80	57.8	63.7	222	38.34	182	25.35	81.81
6	85.00	0.80	58.7	63.9	236	59.21	0.1	4.69	0.04
7	50.00	0.50	59.3	62.8	242	47.78	204	15.06	84.22
8	50.00	0.08	61.3	63.3	251	50.38	209	12.88	83.06
9	15.00	0.20	60.5	62.6	251	49.78	215	12.85	85.87
10	0.50	0.50	58.2	62.5	239	49.43	0.3	13.03	0.12
11	85.00	0.20	59.8	64.5	246	49.24	210	15.21	85.49
12	50.00	0.50	59.5	63.5	237	52.46	207	11.08	87.63
13	50.00	0.50	58.9	65.3	241	49.34	210	15.99	87.33

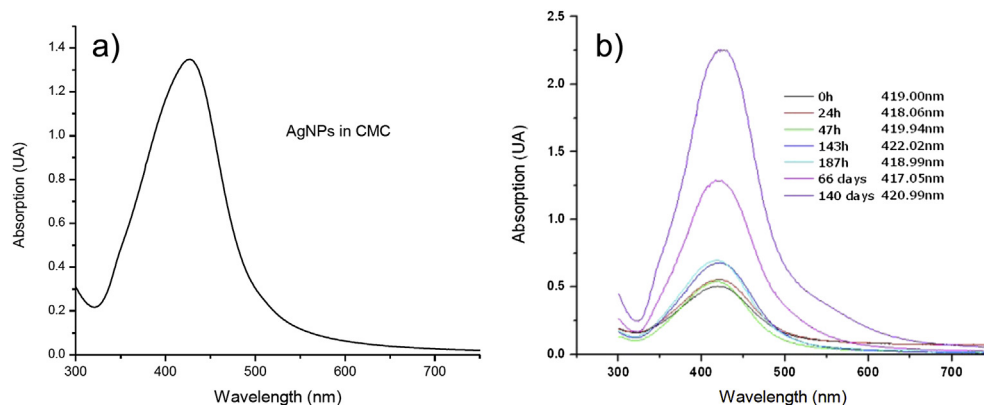


Fig. 1. (a) UV–vis absorption spectrum of AgNPs synthesized in CMC, (b) spectral evolution during long term storage of a colloidal solution of AgNPs.

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