



Cold-crystallization of polyelectrolyte absorbed polyol for long-term thermal energy storage

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ABSTRACT

A lack of efficient crystallization methods and the metastability of supercooled liquids have limited the use of supercooling phase change materials (PCMs) in long-term thermal energy storage (LTES). Here, we propose a new supercooling PCM-polymer mixture that is not prone to spontaneous crystallization during the storage period. The material releases the stored thermal energy by cold-crystallization on re-heating. The PCM-polymer mixture is composed of supercooling polyol (erythritol or *D*-mannitol) dispersed in a cross-linked sodium polyacrylate (PAANa) matrix. PAANa efficiently prevents the conventional cooling crystallization of the PCM. Instead of crystallization, the melt polyol supercools and eventually vitrifies as an amorphous solid. Deeply supercooled or vitrified polyol is stable against crystallization below its cold-crystallization temperature. The heat charged and discharged remained similar in 100 repeated melting-crystallization cycles. Its good long-term performance and the stability of the supercooled polyol-PAANa against crystallization at low temperatures make the new material extremely promising for LTES.

1. Introduction

The intermittency of solar and wind energy continues to limit their use on a large-scale: the variable energy production cannot always meet the demand. To this end, the development of energy storage technologies is crucial [1,2]. Efficient long-term thermal energy storage (LTES) that could store heat for several weeks or months would be highly beneficial, particularly in cold-climate countries where the seasonal variability of solar energy is extreme. Despite its importance, the development of LTES is still in its infancy: the current technologies are based solely on sensible heat storage, in which the heat storage medium is heated without phase changes. Sensible heat LTES require huge storage volumes and efficient insulation. Furthermore, the temperature release levels of sensible heat LTES are often too low for space heating or for the production of domestic hot water [3,4]. Thermochemical storage systems are studied also intensively for LTES. Thermochemical storage is typically based on sorption and desorption processes, which are associated with large amounts of thermal energy. Thermal energy can be stored by keeping the sorbent and sorbate (typically water vapor) apart from each other. The current thermochemical storage materials suffer often from poor stability in cycling and low kinetics, hindering their use in practical applications [5,6].

Third heat storage technology is based on utilization of latent heat,

typically melting and crystallization of phase change materials (PCMs). Upon cooling, melt can either crystallize and release the latent heat, or supercool, i.e. remain in a liquid state below their equilibrium phase change temperature (T_{eq}) [7]. In typical short-term latent heat storage, the PCMs release the latent heat by crystallization close to their melting temperature (T_m). These conventional PCMs can be used e.g. for balancing the daily variation in the environmental temperature [6,8–11].

Many PCMs, such as polyols [12–15] and salt hydrates [16–19], supercool easily. Supercooling is favored if the viscosity of the melt increases rapidly upon cooling and if there are strong intermolecular interactions between the PCM molecules. Conventionally, researchers aim at reducing the supercooling of PCMs for short-term TES [6,12]. However, supercooling may also be exploited in LTES. In that case, LTES is loaded by melting the PCM using e.g. solar thermal collectors or the waste heat of industry. After melting, the PCM can supercool substantially lower than T_{eq} . As long as spontaneous crystallization does not happen, thermal energy can be stored as latent heat and released on demand by triggering crystallization [13–19].

The most studied supercooling PCM is sodium acetate trihydrate (SAT), the supercooling tendency of which was recognized as early as 1895 [20]. Currently, SAT is used in small-scale thermal pads [16,17]. So far, the metastability of supercooled PCMs has prevented their use in large-scale LTES. The stability of supercooled liquids can be improved

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Nomenclature			
ATR-FTIR	attenuated total reflection Fourier transform infrared spectroscopy	W	weight fraction, %
COO ⁻	carboxylate	X	molar neutralization degree of PAANa, %
COOH	carboxylic acid	XRD	X-ray diffraction
DSC	differential scanning calorimetry	ΔE_{T_g}	activation energy for structural relaxation, kJmol^{-1}
EGDMA	ethylene glycol dimethacrylate	ΔH	latent heat, Jg^{-1}
KPS	potassium persulphate	<i>Subscripts</i>	
LTES	long-term thermal energy storage	c	crystallization (cooling crystallization or cold-crystallization) or crystalline state
NaOH	sodium hydroxide	cc	cold-crystallization
NMR	nuclear magnetic resonance spectroscopy	fb, PCM	freezing-bound polyol
PAANa	partly neutralized polyacrylic acid or sodium polyacrylate	fb, H_2O	freezing-bound water
PCM	phase change material	g	glass
SAT	sodium acetate trihydrate	l	liquid
TES	thermal energy storage	m	melting
C_p	specific heat, $\text{Jg}^{-1}\text{K}^{-1}$	nf	non-freezing polyol
k_B	Boltzmann constant, JK^{-1}	PAANa	sodium polyacrylate
m	kinetic fragility parameter	s	solid
q	scan rate, Kmin^{-1}	SAT	sodium acetate trihydrate
R	universal gas constant, $\text{Jmol}^{-1}\text{K}^{-1}$	I	erythritol polymorph I
T	temperature, °C or K	II	erythritol polymorph II
T_{eq}	equilibrium phase change temperature, °C or K	α	<i>D</i> -mannitol polymorph α
T_g	glass-transition temperature, °C or K	β	<i>D</i> -mannitol polymorph β

by the elimination of nucleation centers, such as impurities and rigid container surfaces. However, complete elimination of these factors is extremely difficult, and the probability of spontaneous crystallization increases with increasing volume and storage time [18,19]. In addition, the common crystallization methods used (mixing [15] and addition of seed crystals [14,16,17]) are poorly controlled and ineffective on a large-scale [21].

Spontaneous crystallization of supercooled melt can be avoided if the liquid is cooled below its glass-transition temperature, T_g . Upon cooling, the molecular motion of liquids becomes increasingly slow. The activation energy for molecular motion becomes increasingly high at the T_g when the melt vitrifies as an amorphous solid, glass. Glass is not able to relax into its crystalline state until heated above T_g [7,22–24].

To this end, we show how to exploit supercooling, vitrification and cold-crystallization of a polyol PCM dispersed in sodium polyacrylate (PAANa) for LTES. Vitrification eliminates the principal problem of supercooling PCMs – the risk of spontaneous crystallization. Polyol-PAANa does not crystallize even on slow cooling of 0.05 Kmin^{-1} . Instead, the material supercools and eventually vitrifies as glass. The pre-cooled heat storage material releases the stored energy in the subsequent heating by cold-crystallization. The operation of the new material as LTES is illustrated in the Graphical Abstract.

The influences of the amounts of polyol (erythritol or *D*-mannitol) and cross-linking agent (ethylene glycol dimethacrylate, EGDMA) on the thermal properties of polyol-PAANA are examined. Furthermore, the impacts of the molar neutralization degree of PAANa ($X = 0$ – 1), heating and cooling rates are investigated. Thermal properties of polyols and polyol-PAANA are studied with differential scanning calorimetry (DSC). The polymorphism of the samples is also examined with attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).

2. Materials and methods

2.1. Synthesis of polyol-PAANA

Supercooling *D*-mannitol and erythritol (technical grade) PCMs were supplied by Sigma-Aldrich and Jungbunzlauer, respectively. Acrylic

acid (Merck, Assay $\geq 99\%$) was used as a monomer and potassium persulphate (KPS) from VWR was used as a polymerization initiator. The cross-linker agent, ethylene glycol dimethacrylate (EGDMA) was supplied by Merck (assay $\geq 97.5\%$). Acrylic acid (AA) was (partly) neutralized with NaOH (Sigma-Aldrich). The cross-linker agent links the separate polymer chains together, creating stable three-dimensional polymer network. The network structure decreases the migration of the polymer chains upon polyol melting that would change the PCM-polymer interactions and result in changing thermal properties of the material. The base increases the supercooling state stabilizing ion-dipole interactions between the PCM and the polymer by increasing the charge density of the PAANa.

The mixtures of polyol and sodium polyelectrolyte (polyol-PAANA) were prepared by polymerizing the (partly) neutralized AA in polyol (aq). First, polyol (erythritol or *D*-mannitol) was dissolved in de-ionized water at $\sim 6^\circ\text{C}$ (the mass of the polyol/mass of the water ≈ 1.5), after which the desired amount of NaOH was added to the polyol(aq) (the molar neutralization degree of PAANa, X , was varied between 0 and 1). AA and EGDMA were mixed together at 25°C . The mass fraction of EGDMA, $W_{\text{EGDMA}} = \text{mass of the EGDMA}/\text{mass of the dried sample}$, was varied between 0 and 2 wt%. AA + EGDMA solution was added slowly to the basic polyol(aq) solution at $\sim 60^\circ\text{C}$ before the polymerization. The polymerization of AA was initiated by the dropwise addition of KPS (aq) (KPS + $\sim 1 \text{ ml H}_2\text{O}$) into a well-mixed monomer-polyol solution. The mass fraction of KPS was $\sim 0.1 \text{ wt\%}$ in all samples. The cross-linked polyol-PAANA gel was formed in 5–20 min, depending on the polyol fraction ($W_{\text{polyol}} = \text{mass of the polyol} / \text{mass of the dried sample}$) and the W_{EGDMA} . Water was vapourized from the polyol-PAANA after the formation of the gel by keeping the sample in an oven at 150°C for a few hours. W_{polyol} was varied between 65 and 90 wt% in polyol-PAANA. The sample names and compositions of polyol-PAANA mixtures are presented in Table 1.

2.2. Analysis methods

2.2.1. Differential scanning calorimetry

The melting, crystallization, glass transition and specific heats of the polyols and polyol-PAANA were studied with differential scanning calorimetry (Netzsch DSC204F1 Phoenix DSC and TA 2920, TA

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