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Thickening and Gelling Agents for Formulation of Thermal Energy Storage Materials – a Critical Review

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Abstract

Thermal energy storage is a promising approach for alleviating the mismatch between the energy supply and demand, utilizing renewable energy sources, exceed electric and industrial heat. Thickening and gelling agents are additives used in thermal energy storage area to address the stability and shape stabilisation of thermal energy storage materials, which are main challenges in thermal energy storage technology deployment. This paper is the first comprehensive review of thickening and gelling agents used in thermal energy storage (TES) applications. An insight is provided regarding recent progress in this area, covering the classification and mechanisms of the thickening and gelling agents, The impact of the thickening and gelling agents on the physical properties of different fluids is discussed to further address the role of thickening and gelling agents in the field of TES. Following the discussion of the state of the art of thickening and gelling agents in TES, a standard preparation methodology and associated evaluation process are proposed with the establishment of a thickening and gelling agent database which provide a guidance for the screening and formulation of composite TES materials. Even though the thickening and gelling agents have a promising role in enhancing the TES system performance, further investigations are needed to tackle the issues that limits their usage such as cost and standardisation.

Highlights

- Reviewing and classifying the different thickening and gelling agents available in the literature used in different applications
- Assessing and discussing the possible materials available in the literature that could be used in thermal energy storage technologies
- Generating a data base of the thickening and gelling agents, listing their main characteristics that need to be considered in use/have significant effect on the mixtures
- Providing a selection tree to help to identify possible thermal energy storage thickening and gelling agents depending on the working temperature and base fluid characteristics
- Reviewing and highlighting the effects and challenges of using thickening and gelling agents in thermal energy storage

KEYWORDS: thermal energy storage; phase change material; thickening agents; gelling agents; form-stable

Word count: 8889

List of abbreviations

CMC Carboxymethyl cellulose

HPEC Hydroxypropyl ether cellulose

PCM Phase change material

PAAm Polyacrylamide

SAT Sodium acetate trihydrate

SAP Super-absorbent polymer

TES Thermal energy storage

TCM Thermochemical material

1. Introduction

Thickening and gelling agents are additives that create stiffness, stabilize emulsions or form gels when dissolved or added into a dispersing phase. Depending on the agents used, the thickening effect varies from low viscosities at a fairly high concentration to high viscosities at concentrations below 1% (majority).

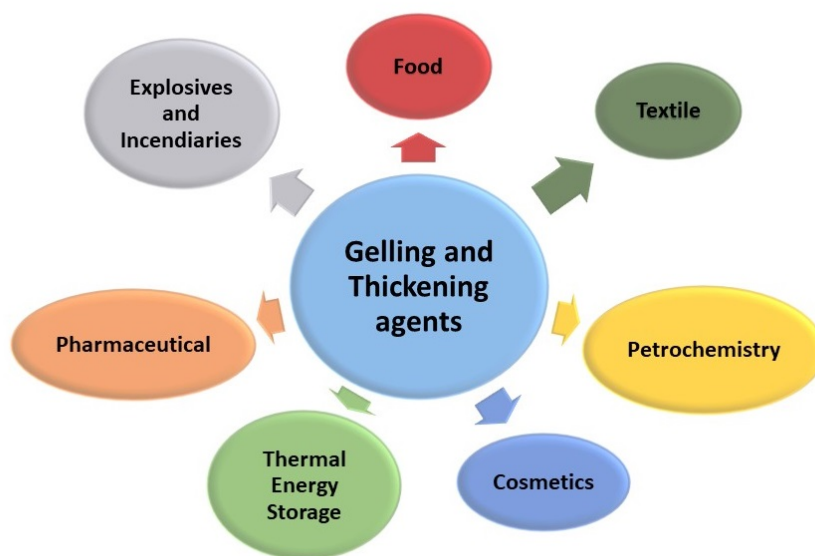


Figure 1 Applications of thickeners and gelling agents

Thickening and gelling agents play a key role in many industrial sectors [1] [2]; see Figure 1 for a summary. In the pharmaceutical industry, they are used to make stable semisolid formulations (e.g. gels for easy spreading by pressure or friction to deliver drug dosages externally [3]). They are employed in the food industry for making soups, gravies, salad dressing, sauces, and jams to restructure the food material and provide food a particular texture, taste, and mouthfeel that improve the overall eating experience [4]. Fine chemicals is another important sector where thickening agents provide a method to tailor the rheological properties and improve stability, feel and flow [5]. Thickeners and gelling agents have also been used in textile colorants and paints; an example is the use of polyacrylic acid as thickener for textile printing. In the petroleum and explosives sectors, guar gum and its derivatives are used in the fluid's fracturing process to help keep the proppants within the fluid [6].

The use of thickening and gelling agents in thermal energy storage (TES) for improving thermal performance has a low visibility so far, although this has been ongoing for more than 20 years (relatively new compared with hundreds of years in other areas of applications). Thermal energy storage is traditionally classified into sensible, latent and thermochemical storage [7], as shown in Figure 2. Sensible storage materials store thermal energy by changing material temperature, and the energy stored in a sensible storage material depends on its specific heat and the operation temperature range. Latent storage materials store thermal energy through an isothermal process during phase change (solid-solid, solid-liquid,

etc.) and are therefore also called phase change materials (PCMs). PCMs in practical applications mainly utilise phase change transitions considering the balance between thermal energy stored and complexity of the system design. Thermochemical storage materials store thermal energy through reversible chemical reactions and/or sorption processes.

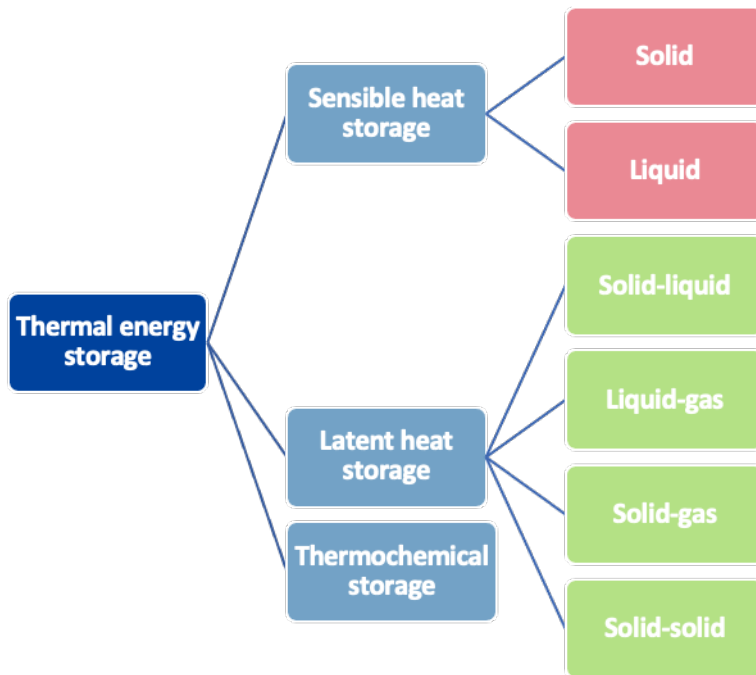


Figure 2. Overview of thermal energy storage technologies with a specific focus on materials [8,9]

At the material level, TES currently faces several profound challenges which can be addressed by using thickening and gelling agents, particularly those related to stability (phase segregation) [10], supercooling [11], leakage, shape stability and volume change. However, the impact of the use of thickening and gelling agents is a double-edged sword as their introduction can also result in reduced crystallization and heat transfer in some cases [12].

1.1 Thickening and gelling agents for thermal energy storage materials

Challenges in TES materials that affect their performance and industrial uptake are associated with their reliability which depends on their physical and chemical stabilities during cyclic charging/discharging processes. Strategies to tackle these challenges are currently being studied and assessed. Some of them involve the incorporation and optimization of thickening and gelling agents in TES material formulations with the aims of preventing composition segregation, minimising volume change, and achieving leakage-free/shape stability.

1.1.1 Cycling stability

Incongruent phase change or phase segregation is one of the main challenges that a latent heat based TES material (PCM) often occurs during thermal cycling. For instance, in a salt hydrate solution, when it is supersaturated with the salt in the liquid phase, solid salt crystals are formed, and sediment at the bottom of the container due to gravitational force. During discharging, water-rich phase at the top of the solution cannot be bound with salt at the bottom to form the salt hydrate that leads to phase separation after thermal cycling. The

addition of thickeners and gelling agents has been studied to reduce solid to reduce solids settling [13].

1.1.2 Supercooling

Supercooling describes the postponement phenomena of crystallisation during a liquid-solid phase change. The degree of the supercooling is the temperature difference between the melting and the freezing temperature as follows:

$$DT_s = T_m - T_f$$

where DT_s denotes the degree of supercooling, T_m is the melting temperature and T_f is the freezing temperature.

This phenomenon significantly affects their industrial applications where a narrow and accurate working temperature range is required. Solutions to reducing/eliminating supercooling to enable energy release when needed are often based on how the phase change/crystallisation is triggered; see Figure 3 for an illustration.

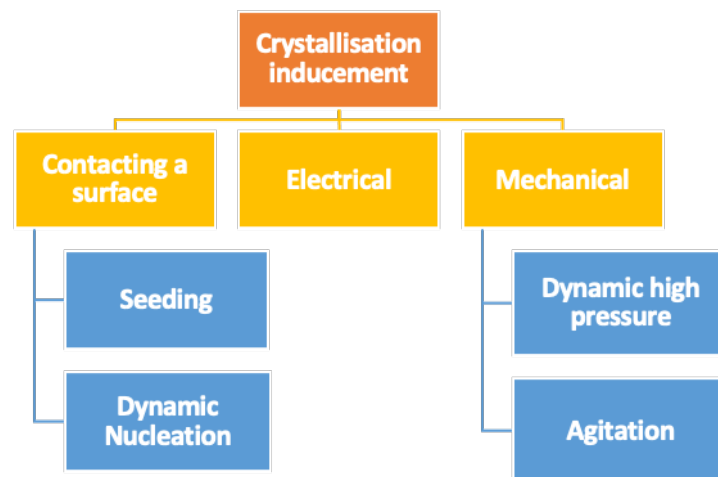


Figure 3 Methods to induce crystallisation event [14]

The mechanisms of inducing crystallisation in a subcooled liquid can be broadly classified into three categories: surface contacting, electrical and mechanical inducement. Surface contacting is the most common and effective ones, especially the seeding method. Seeds act as nucleators that helps the system to overcome the nucleation energetic barrier and initiate crystallisation event. The introduction of thickening/gelling agent have a remarkable impact on the supercooling degree of stable compounds over charging/discharging cycles. Kensarin et al. [15] studied sodium acetate trihydrate (SAT), an abundant and low cost PCM candidate. The use of thickeners and nucleating agents results in a low degree of supercooling, 5°C and a good chemical stability after 1000 cycles.

1.1.3 Immobilisation

Thickeners and gelling agents have been used to formulate composite PCMs to achieve a high viscosity and form-stability during thermal cycling. Gel is a three-dimensional network that can hold the fluid within its semi-rigid structure [4] and hence prevent leakage. Saeed et al. [16] prepared a form-stable gel using a methyl palmitate/lauric acid mixture as a PCM,

graphene nanoplatelets as a thermal conductivity enhancer and 2-hydroxypropyl ether as the gelling agent, and demonstrated the form-stability.

Large volume changes during a phase change or a thermochemical process affect the mechanical properties of TES materials as well as the device design. Take the device design as an example, the volume change implies the TES device need to accommodate expansion/contraction, which can complicate the design affect the cost. Hua et al. [17] studied the use of different thickeners for sodium acetate trihydrate based PCM formulation, and found that they can not only prevent the phase segregation, but also reduce the volume change of the composite to around 5%.

1.2 Scope and structure of the review

As mentioned earlier, although there have been lots of studies on the thickening and gelling agents in various industrial sectors and a few reviews related to food [18] [19], cosmetics [5] and pharmacy [20], they are far from comprehensive with little information on composition and mixing process and their effects on the final mixture. In the TES field, the use of thickening and gelling agents has not been systematically assessed, not their optimal use. This article aims to provide a comprehensive review with a specific focus on the use of thickeners and gelling agents in thermal energy storage materials for the first time, covering the following:

- Thickening and gelling agents are classified in Section 2 according to their main characteristics. A corresponding database is established for the first time to guide the agent selection process.
- Three different mechanisms are highlighted in Section 3, providing a fundamental understanding for the thickening/gelling behaviour.
- Section 4 and Section 5 then assess and discuss the use of these agents in TES, followed by a selection tree to help identify possible TES thickening and gelling agents based on the working temperature and base fluid characteristics
- Finally, reviewing and highlighting the effects and challenges of the use of thickening and gelling agents in TES materials in Section 6 provide a comprehensive review in the field. An outlook is given to the future use of thickener and gelling agents in the TES field.

2. The classification of thickening and gelling agents

Thickening/gelling agents can be classified based on their sources, thickening mechanism, degradability, etc [21]. Figure 4 shows a classification based on their sources, that the thickening/gelling agents can be divided into three main categories of synthetic, semi-synthetic or natural sources. These categories are further sub-classified according to their chemistry properties, either organics or inorganics. A few representative candidates under each category are listed. Most agents are organic except for those from minerals. Exudates, seeds, microbial polysaccharides, animal extracts and pure plant extracts are all very popular thickening and gelling agents in industry. They are also abundant as all of them are nature material. Synthetic and semi-synthetic agents are mostly polymers with different functional groups while semi-synthetic agents are modified nature materials.

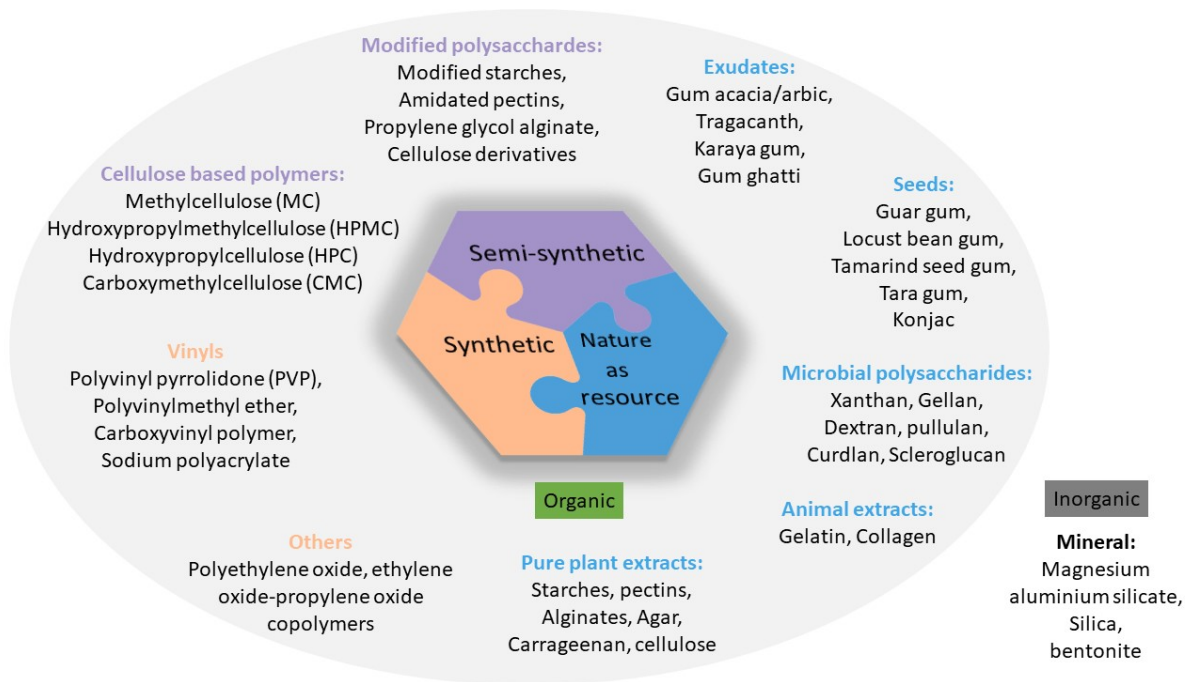


Figure 4 Classification of thickening and gelling agents [22]

Table 1 lists the properties of well recognized thickening/gelling agents. The most commonly used thickening/gelling agents are listed in the table and classified by their type - whether they can act as a thickening, gelling, emulsifier or a stabiliser agent; by their solubility in water; by their ionic exchange and structure; and by their applications: food, cosmetics, pharmaceutical, textile, printing/packaging or petroleum industry. Besides, a column of the table is dedicated to specifying the compatibility and incompatibilities with other materials and another to parameters affecting the workability and formation of the agents. This is to give an overview of the preparation of the agents and the prediction of their performance under practical conditions. In this regard, the reversibility of the agent-type of transformation is also compared in Table 1 as reversible, irreversible, or subjected to other effects (e.g. shear-thinning, pseudoplastic, etc).

Most of the agents listed have good solubility in water regardless of the type and the ionic charge except that carrageen, agar and cellulose derivates are only soluble in water at relatively high temperatures (above 70 °C). All anionic agents are reversible whereas most of the non-ionic agents are irreversible. Because the ionic type data of some agents are missing, a more comprehensive analysis is only possible after further investigations are made. The mechanism of this phenomenon should be studied in the future. The percentage normally used are ranged from minimum to maximum, those are normally up to 5 wt. %, which indicates that with a small amount of the agent, the rheological property of the solution is significantly changed. Amongst all the agents, Agar, Pectin and Carrageenan function at the ratio of less than 1 wt. %, making them widely used in many industrial areas such as food, leather, textile, pharmaceutical and healthcare. Except for Xanthan gum which is only used in food industry, all agents work in food and Pectin industries. Only cellulose derivatives and modified starch are currently used in cosmetic industry and cellulose derivatives is the only agent used in petroleum industry. Printing/packaging/paper coating sectors requires excellent stability of the agents and exudate, seed gum are used in this area.

The most versatile agent is seed gum as it can be used as thickening, gelling, emulsifier, and stabiliser agent. This will be explained in depth in the following sections for each of the agents described.

Table 1 the properties of commonly used thickening/gelling agents

Agent	Type	Ionic charge	Structure	Solubility	Application usage (ratios)	Compatibility	Factors affecting the properties	Performance
Agar [4,23,24]	T, G, S	-	Heteropolymer/linear	Water soluble in boiling water	F, P, L 0.2-2%	√ locust bean gum, high sugar concentrations (~60%) x with oxidizing agents/proton, scavengers, urea and guanidine will block the gelling process by impeding the formation	Not suitable for acidic conditions (pH<4)	Reversible
Alginate [4][25][26]	T, G, S	-	Homopolymer/heteropolymer linear	Water soluble	F, P 1-2%		Associated solution, alginate molecular length	Irreversible/shear-thinning
Cellulose derivatives [23,27-30]	T, S	E, anionic	Homopolymer	Water soluble in boiling water	F, P, C, O 1-4%	√ compatible with a wide range of natural and synthetic water-soluble polymers x Possibly salt-out at high temperature or inorganic salt concentrations	Present of salts/the order of addition	Reversible with condition/pseudoplastic
Carrageenan [21]	T, S	G, anionic	linear	Water Soluble at temperatures	F, P 0.5-3%		associated salts	Reversible

[25][31][32]					above 70°C			
Exudate gum [23,24,31]	T, E	-	Heteropolymer	Water soluble	F, P, L, D 3-5%	√ compatible with most gums and starches x sodium alginate, agar gels, microbial	Particle size, material mesh and heating time	Reversible/pseudoplastic
Modified starch [4,24,33]	T, S	G, Non-ionic		Water soluble	F, C, P, I		Gelling spread, steric, ionic, covalent or electrostatic effects	Irreversible/shear-thinning
Pectin [31][24]	T, S	G,	Heteropolymer/ Linear (branched)	Water soluble	F, P 0.1-4% (low methoxy) 2-4% (high methoxy)	√ alginate at PH<4 x generally no compatible with other hydrocolloids	Mixer speed, temperature	Reversible for low methoxy pectin / pseudoplastic
Seed gum [23,31,33][4][34]	T, E	G, S, Non-ionic	branched	Water soluble	F, P, L, D	borax, calcium/ xanthan gum, locust bean gum and sodium alginate (synergistic)	Temperature/ vigorously shaken	Shear-thinning
Xanthan gum [4,23,27,33, 35]	T, G	Highly anionic	Heteropolymer	Water soluble	F 1-3%	√ high concentrations of salts, most acids, thickeners (starch, carrageenan,	Temperature up to 300°C	Reversible pseudoplasticity/ high shear-

cellulose derivatives, gelatin
and alginates)

thinning

x dairy proteins, if the
system is acidic or heat-
processed

T: thickening agent

G: gelling agent

E: emulsifier

S: stabilizer

F: food

C: cosmetic

P: pharmaceutical & healthcare

L: leather & textile

D: printing/packaging/paper coating

O: petroleum industry

2.1 Agar

Agar is a seaweed hydrocolloid, or phycocolloid with a long history of use as a gelling, thickening and stabilising food additive [24]. Agar is insoluble in cold water but can be hydrated to form random coils in boiling water (melting point 80-90°C). As is shown in Table 1, the agar gelation process is reversible, which means the gelation state can withstand repeated heating/cooling without significant change in the mechanical properties. When the pH is below 4, or oxidising agents exist in the system, agar stops functioning. Agar forms gels at a concentration of around 0.2%. The gel strength is strongly influenced by concentration, pH and sugar content. High sugar content (>60%) has shown to enhanced the gel strength [24].

2.2 Alginates

Alginates are reported as one of the most significant hydrocolloids used in food, which is extracted from brown seaweeds. It is a versatile agent as it can be used as thickening, stabilising, gelling and film-forming agent and it is soluble in both hot and cold water. Researchers reported that the dissolution rate depends on the particle size of the alginates. Smaller particles dissolve fast and have higher chance to agglomerate and form lumps [36]. With the presence of calcium ions promote the formation of a stable cold-setting gel network which allows it to work at a wider range of temperatures [23]. The alginates gel is particularly resistant, shear irreversible and heat stable [24]. However, alginates solution exhibits shear-thinning properties and it is affected by the composition of solution system because of the molecular weight redistribution of alginates.

2.3 Carboxymethyl cellulose (CMC)

Carboxymethyl cellulose (CMC) is a cellulose derivative commonly used as a thickening agent, stabilizer and emulsifier. It has been intensively applied in the TES fields especially the cold energy storage systems[37][38]. Like alginates and guar gum to be introduced in 2.5, CMC is also soluble in both cold and hot water. The rheological behaviours of CMC in aqueous dispersions depend on the factors such as concentration, molecular weight and degree of substitution. When the powder formed CMC contacts water, the particles tend to agglomerate because of the rapid hydration of cellulose gum [24]. With the presence of divalent and trivalent ions, CMC forms weak gels at above 52 °C. The polymer chain length affects the viscosity and solubility of CMC. Shortening the chain will increase solubility and decrease the viscosity [24]. The presence of salt affects the cellulose gum solutions. Monovalent salts have little impact on the solution characteristics while divalent salts have significant impact on it. Therefore, CMC should be fully hydrated before the salt is added.

2.4 Carrageenan

Carrageenans are polysaccharides (galactose) with various degree of sulfation (between 15% and 40%) [39]. They are extracted from red seaweeds and can be used as thermo reversible gelling agents and thickening agents. There are three main commercially available classes of carrageenan: kappa, iota, and lambda. They are all soluble in hot water, but only the lambda form is soluble in cold water without forming a gel. Only iota/lambda are soluble in salts. Among them, κ -Carrageenan is the most used, while λ -Carrageenan is the least utilized because it is very expensive to produce [40]. The gels formed by ι -carrageenan have

much more flexible textures and are less sensitive to shearing than the others. Iota network is formed by a series of double-helices and kinks form a transparent, elastic gel [24]. Mechanical disturbance can easily break this loose network. However, the network reforms quickly once the mechanical disturbance ceases. The gels formed in the solutions of κ - and ι -types upon cooling. They are stable at room temperature, melt by heating and recover upon cooling without loss of gel strength or texture in neutral conditions [22].

2.5 Guar gum

Guar gum is a polysaccharide of galactose and mannose, which is obtained from the plant *Cyamopsis tetragonoloba* [39]. This agent can be dissolved in both hot and cold water. The gelling capability of guar gum is considered weak, which makes it mostly studied as thickening substance. The gel structures unstable at the temperature above 90 °C and pH values below 3.5 because of the depolymerisation [24]. As a thickening agent, it presents a high viscosity at low concentrations. The addition of borate ions to guar gum solutions causes the increase of gelation rate. The addition of monovalent cations have no effect on its thickening ability, while an addition of di- or trivalent cations also leads to a viscosity increase. However, its viscosity is decreased with the addition of polyols. Besides, the addition of guar gum to gelling polysaccharides such as agar increases the strength and elasticity of the gels [22].

2.6 Gelatine

Gelatine is a collagen material obtained from animal tissues. It has been used in a wide range of food and pharmaceutical applications. Commercial gelatine products vary from the form of fine powders to flakes. In general, it shows high solubility in water as it can absorb 5-10 times its own volume of water. Gelatine solution is in general considered not viscous, although it shows Newtonian fluid behaviours above 40°C [24]. The viscosity of gelatine solution depends on a range of parameters: temperature, concentration, ionic content and pH. The gelatine gel is thermoreversible. The melting point of it is as low as 37°C.

2.7 Modified Starch

Starch is one of the most important polysaccharides and is a major component of many plant-based food such as wheat, corn, potato, etc. Modified starch is available in various of range and differentiated grades based on the type of the raw materials and the production process [24]. Starch is used in a very wide range of applications such as food, cosmetics, paper, textile, and certain industries, as adhesive, stabilizer, thickening and gelling agents. When the temperature increases over the thickening point of the starch, the suspended starch granules swell and absorb water until reach the maximum volume. A gel-like structure is then formed with heating.

2.8 Polyacrylamide

Polyacrylamide (PAAm) is a commonly used non-ionic water-soluble polymer in pharmaceutical, cosmetic and oil recovery applications. PAAm is formed by polymerization of acrylamide with either inorganic crosslinkers (e.g. chromium) or organic crosslinkers such as phenol and polyethyleneimine [41]. The viscosity of PAAm solution is sensitive to high

temperature and inorganic salts. The latter is caused by the reaction between salt and carboxylic group that hydrolysed from amide groups when presented in aqueous solutions [42]. It can remain chemical stability in various conditions.

2.9 Xanthan gum

Xanthan gum is a long-chain polysaccharide produced commercially in a batch fermentation process [24]. Given its soft texture, xanthan gum is widely used as a thickening agent or viscosity modifier in both food and non-food industries. Therefore, most of the studies are focused on Xanthan's thickening property while it is considered both a thickening and gelling agent. It can also work as a stabilizer in a wide variety of suspensions, emulsions and foams. It can be dissolved at room temperature, while hydration time is reduced with the increase of mixing speed, temperature and higher particle sizes. It is recommended to hydrate xanthan in water before adding salt in the mixture because xanthan has very good salt tolerance (up to 20–30% salt) while it is hydrated. Besides, xanthan has a great stability over a wide pH (2.5-11) and temperature range (up to 300°C). Owing all the pros it is widely used in TES applications [37][43]. However, the biodegradation and mildewing issues of xanthan require more attention.

3. Thickening and gelling mechanisms

Thickening agents are additives used to increase the viscosity of a fluid, whereas gelling agents are added into a fluid to form a structure called gel. According to IUPAC, a gel is a non-fluid colloidal network or polymer network expanded throughout its whole volume in a fluid that has a finite (generally small) yield stress [44]. Attributed to the cross-link mechanism gel can be formed through physical or chemical interaction [45].

As is discussed in Section 2, the distinction between thickening and gelling agent can be sometimes difficult to define, as a limited cross-linking process can also thicken the solution [23]. The extent of the thickening achieved is affected by the thickening behaviour of the material used, the suspending medium, ions concentration, temperature and pH [4]. By varying those factors, the flow properties of the dispersing medium can be changed to achieve the required properties. In this paper, the different mechanisms of thickening and gelling are discussed in detail.

Gelling and thickening additives modify the rheological properties of the solution, which can be attributed to different mechanisms, depending on the chemical nature of the additive. As shown in Figure 5, three different mechanisms are listed: non-associative, associative (physical), and chemical. Thickening agents follow non-associative or associate (physical) mechanisms. Gelling cross-linking can be formed depending on the dominant mechanism, with strong or weak interactions. Weak ones refer to the physical interactions, whereas the strong ones are chemical interactions in the formation of covalent bonds [46].

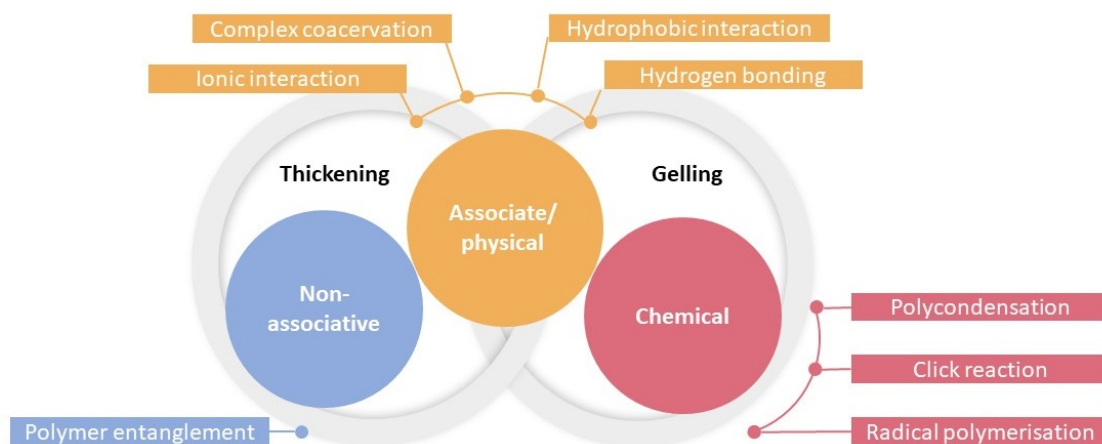


Figure 5 Cross-linking methods for chemical gelation

3.1 Non-associative mechanism

According to the non-associative thickening mechanism, the thickening of the fluid occurs through the entanglement of high molecular weight polymer chains, (hundreds of thousands to several million) which determines the thickening efficiency. The entangled continuous phase and volume expansion result in an increase of the viscosity. This may cause the dispersed components to displace from the continue phase due to volume limit, and in some cases leads to particle flocculation. Non-associative thickeners are normally low-cost common materials from natural resources. These solutions normally have pseudoplastic behaviour and highly elastic properties [47].

3.2 Associative/Physical mechanism

Associative thickeners are water-soluble or water-swellaible polymers that contain several hydrophobic groups spaced along the polymer chains. It has a relatively low molecular weight compared to non-associative thickeners. A sufficient amount of hydrophobic end functional groups of the thickener are polymerized with other hydrophobic substances to form an overall net-link structure which increase thickening power. The behaviour of the associative thickeners changes significantly with the associative group, a stronger associative interaction will lead to higher viscosity.

Gel physical cross-linking can be classified into hydrophobic interaction, hydrogen bonding or ionic interaction (or combinations of them) or complex coacervation. These gels are reversible and their strength is affected by the experimental conditions such as temperature or pH. Ionic interaction mechanisms are the ones that use di- or trivalent counter anions to crosslink the polymer. The counter ion concentration will affect the amount of crosslinks formed, hence the strength of the gel. Hydrogen bonding gels can be formed by modifying the pH or temperature of an aqueous solution where the polymer is dissolved [48]. Hydrophobic interaction refers to the formation of the gel due to the repulsion of the functional groups in the polymer, between hydrophobic and hydrophilic groups in the right experimental conditions. Complex coacervation is the formation of gels due to the interaction

of cationic polymers and anionic polymers, which interact together to form the gel network [49].

3.3 Chemical mechanism

Gels chemical cross-linking occurs when the polymer chains have functional groups able to react and form covalent bonds. Depending on their nature and functionalization, the gels can be further categorised by their cross-linking method.

Radical polymerization involves the formation of free radicals activating an initiator (light, temperature, or redox reaction) that leads to the formation of the polymer network. However, the chain polymerization can form a non-homogeneous gel structure which leads to inferior mechanical properties. Polycondensation refers to the obtention of polymers from bifunctional and polyfunctional monomers and the elimination of low-molecular weight by-products (e.g. water or alcohols). Click reactions are high efficient (high regio- and chemoselectivity), have a moderate reaction temperature and have a fast reaction kinetics [50]. They can be used to form gels that are highly compatible with bioactive compounds, which make them suitable for biological applications [51].

4. The impact of the thickening and gelling agents on material physical properties

The use of thickening/gelling agents has profound effects on complex materials' physical properties, particularly rheological behaviour and stability, which are discussed in detail in the following sub-sections. Although these are essential for the TES application, little attention has been paid on these impacts in the TES field.

4.1 Rheological behaviour

The viscosity enhancement is one of the most important effects of thickening/gelling agents. In this respect, the viscosity increment of the fluids ascribed by different mechanisms causes a change in the rheological properties of the TES material. Considering the rheological effectiveness of thickening/gelling agents, they can create three overall rheology profiles: Newtonian, shear thickening (dilatant) and shear thinning (pseudoplastic, also called thixotropic). Their correlation between shear stress and viscosity is presented in Figure 6.

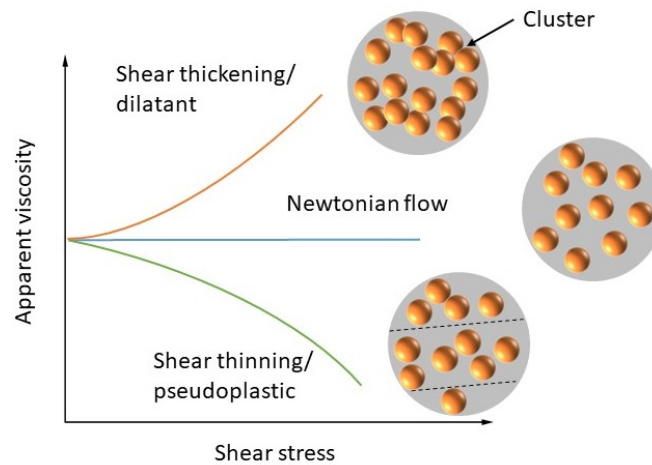


Figure 6 The rheological behaviour of complex fluid systems [52]

The rheological behaviour of a thickened liquid can be complicated. It is affected by the conformation (particle size, shape, aggregation), quantity of the thickening/gelling agent chains, shear rate and agitation conditions. For instance, it is reported by Song et al. [53] that xanthan gum solution exhibits a significant viscosity enhancement with increasing concentration and a marked shear thinning behaviour at high concentrations. It also is related to the presence of other substances, working condition such as temperature, and pH, etc. For instance, the viscosity of the aqueous starch solution keeps increasing owing to the continually swelling granules until 90°C, whilst further increase in temperature will result in a viscosity decline [54].

4.2 Operational condition

The introduction of thickening/gelling agents increases the viscosity and stability of the system, prevents separation and, possibly controls the crystal formation during phase change [24]. As mentioned in the previous section, besides the agent type and concentration, suitable operational conditions are required for the thickening/gelling agents to achieve the best performance. Figure 7 shows the temperature/pH range for thickening/gelling agents. Beyond this range, the decrease in viscosity or system decomposition will occur. It is reported that the thermal degradation of the system is governed by three factors: macromolecular motion, solubilisation and molecular weight decreasing [55]. In addition, when using multi-agents, the compatibility of each agent can influence the system stability. The compatibility information of some commonly used agents can be found in Table 1.

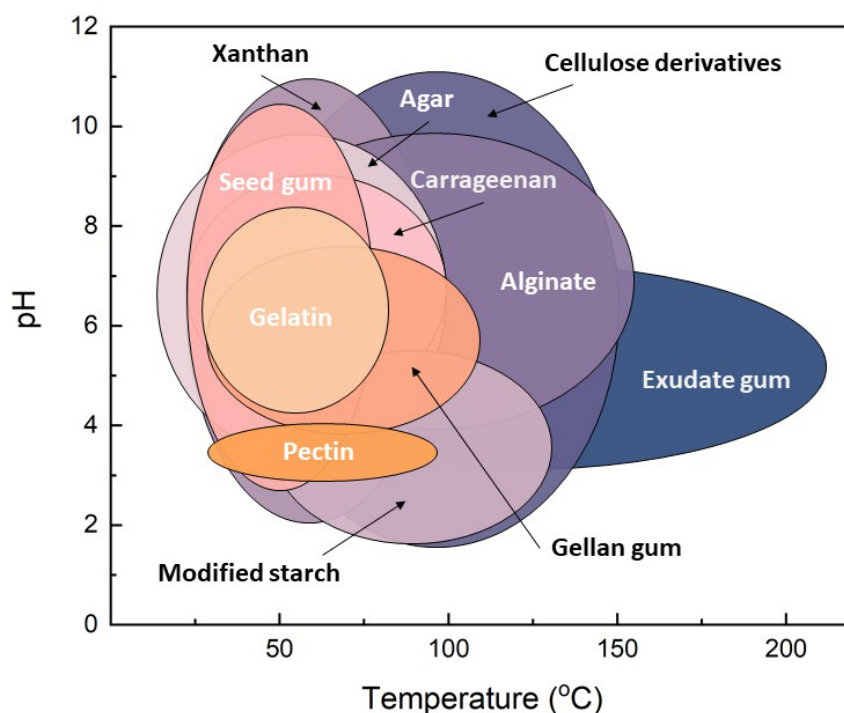


Figure 7 The temperature/pH range for some commonly used thickening/gelling agents

5. Thickening/gelling agents in thermal energy storage

5.1 The state of the art

As mentioned earlier, phase separation and incongruent melting have been affecting the practical implementation of TES technologies in many cases [35]. To address these issues, efforts have been made to immobilise TES materials by adding thickening/gelling agents. This section reviews a substantial number of papers relating to the use of thickening/gelling agents in the thermal energy storage sector. This section reviews a substantial number of papers relating to the use of thickening/gelling agents in the thermal energy storage sector. A summary is provided in Table 2 regarding the agents used, the base PCM, the working temperature, concentration used, preparation method, performance, cycling stability and thermal conductivity (when available).

A systematic approach of screening thickening/gelling agent for improving the performance of TES materials is not yet available and it is affected by several factors. Therefore, different combination of the TES materials and thickening/gelling agents are studied by researchers. Ryu et al. [30] first studied the interaction of various salts with different thickening agents: super-absorbent polymer (SAP), CMC and potassium sulfate. SAP was found to be the most suitable thickening agent to prevent segregation of hydrate inorganic salts, whilst CMC was more effective for SAT. The use of some thickening agents, such as bentonite clay (added to Glauber salt) has been suggested to overcome the problem of phase segregation, which will bring in unwanted side effects such as reduced thermal conductivity that given the lower crystallization and heat transfer rate of the mixture [12]. Efimova et al. [56] prepared stable new ternary eutectic salt hydrates (zinc nitrate hexahydrate, manganese nitrate tetrahydrate

and potassium nitrate) through the incorporation of a nucleating agent and thickening agents. They explored the use of three different thickening agents: silicon dioxide, xanthan and methylcellulose (3% in weight). Silicon dioxide showed a poor performance after a few cycles; the mixture with methylcellulose has high viscosity after cycling but showed significant phase segregation; the only sample that showed no visible segregation was the one containing xanthan. Thus, xanthan stabilizes the PCM system without phase segregation while silicon dioxide and methylcellulose decrease the enthalpy fusion and increase the supercooling effect.

Xanthan and CMC are two thickening/gelling agents that have been frequently used in the TES field. Xiao et al. [57] applied vacuum impregnation to fabricate SAT-xanthan copper form thermochemical material (TCM) module. The stability of TCM was enhanced greatly with the presence of 2 wt.% of xanthan gum. A more than 30°C of hysteresis reflected in the degradation temperature comparing with the pure TCM. The heat capacity of the module only reduced 5.9% after 200 melting and solidification cycles. Dannemand et al. [27] added xanthan to avoid the deposition of sodium acetate in the sodium acetate/water mixture. The thickening agent will help recombine the sodium acetate to the nearby water molecules during crystallisation process to form SAT, thus decreasing the phase segregation of the PCM. It was mixed with 2-3 g of crushed SAT before added into the melted mixture of SAT and graphite, to ensure that the xanthan was properly dispersed. The PCM complex with xanthan/graphite showed more discharge cycles and higher heat transfer rates than simple substance SAT, while no phase segregation was observed. The research also demonstrated that the performance of different thickening/gelling agent in the same TES material can be different. A least 5% of CMC or 1% of xanthan is required for a sufficient thickening effect in the SAT-graphite PCMs. Upon solidification, composites with CMC exhibit large cavities or big cracks, and yet large number of small cavities distributed within composites containing xanthan, as shown in Figure 8. These cavities have significant impact on the thermal conductivity of the SAT composite. Similar study was also conducted by the same group regarding the combination of SAT and CMC [58]. This study concluded that 1% CMC was the minimum quantity to achieve a stable and uniform mixture.

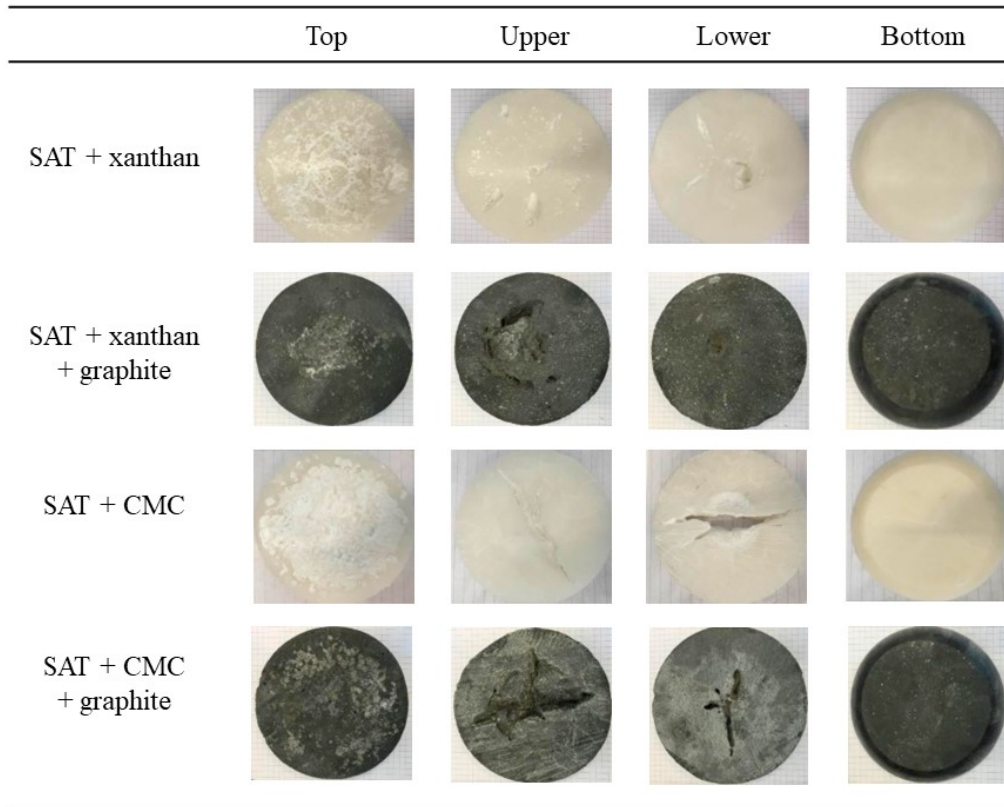


Figure 8 The view of cavities in different SAT complexes, Figure adapted from Dannemand et al. [27]

Xiang Li et al. [59] studied the thickening effect of CMC in SAT-KCl-Al₂O₃ composites. The study demonstrated that the energy storage density decayed by 3.6%, and particles distributed homogeneously within composites after 50 cycles. Wang et al. [60] applied CMC (1.5 wt.% regarding the TCM) during the encapsulation process of erythritol. Erythritol was mixed with the surfactant followed by the addition of the CMC and nucleation agent. Then the precursor of shell material and other additives were added subsequently. Then, an ultra-turrax high speed homogenizer and ultrasonication cleaner were used to further disperse the mixture respectively to form a water in oil (W/O) emulsion. After the process, the encapsulated erythritol composites underwent 200 thermal cycles. Capsules contain an average of 59 wt.% erythritol have shown favourable thermal properties with a 213.3 kJ/kg of energy density upon melting at 121.2°C, an 83.6% on supercooling depression, 29.2% of increasing on the thermal conductivity and excellent thermal stability. Zou et al. [61] reported, CaCl₂·6H₂O based composite was stabilized using 2% of methyl cellulose for air-conditioning application purpose. Results from the DSC measurements proved that no significant variation on the phase change temperature and energy density of the PCM along 50 thermal cycles. The supercooling degree increase to 3.5 then maintain unchanged.

In addition to xanthan and CMC, Fu et al. [62] demonstrated that the combination of sucrose and fume silica can effectively suppress the phase segregation in SAT-urea systems, as shown in Figure 9. 2% of sucrose was mixed with the binary PCM and nucleating agent thoroughly in a seal container and heated up to 60°C. The melted mixture was mixed with 30 wt.% of fumed silica (SiO₂), then cooled down to form composite TCM. Fumed silica acted as both structure supporting component and temperature regulator, also contributed greatly on

the TCM stability. The energy storage capacity, physiochemical stability and crystallization behaviour of the TCM composite had minor variations after 200 cycles.

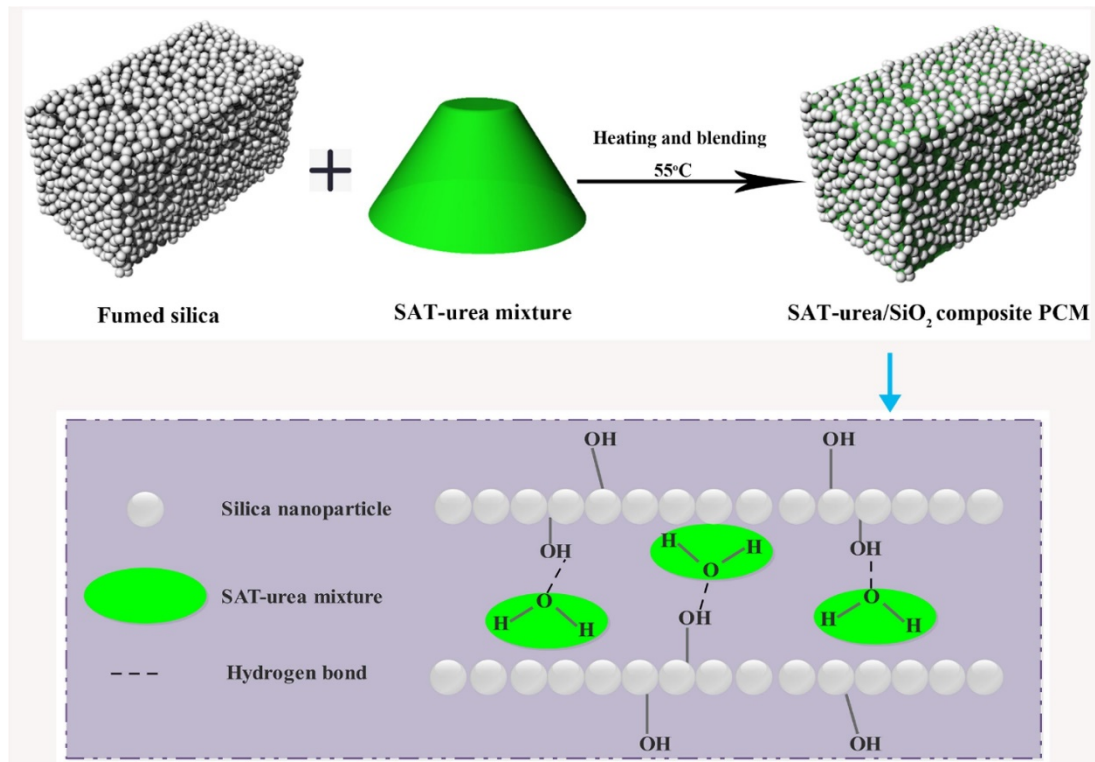


Figure 9 The formulation of SAT-urea/SiO₂ composite PCMs, Figure from Fu et al. [62]

Saeed et al. [16] introduced a different cellulose, 2-hydroxypropyl ether cellulose (HPEC), to form a shape-stable form with a binary eutectic methyl palmitate-lauric acid mixture, which solved the liquid leakage problem. HPEC was mixed with methyl palmitate and lauric acid (60/40) based PCM at 50°C, as shown in Figure 10. Then the mixture was heated up to 70°C to achieve a better fluidity before dispersing nano-graphene platelets. Results suggest that 7.5 wt.% is the optimal mass fraction of HPEC in the mixture because only all composites containing more than 7.5 wt.% of HPEC exhibit form-stable gel texture appearance. The leakage occurs when the HPEC mass fraction is below 7.5 wt.%. The thermal analysis shows HPEC did not alter the congruent melting behaviour of the eutectic PCM, and a reduction on the supercooling degree was also attained. Although the melting temperature, energy storage density and thermal conductivity of the complex had a minor decrease with 10 wt.% of HPEC, an outstanding reliable thermal performance was observed over 30 thousand thermal cycles, see Figure 11.

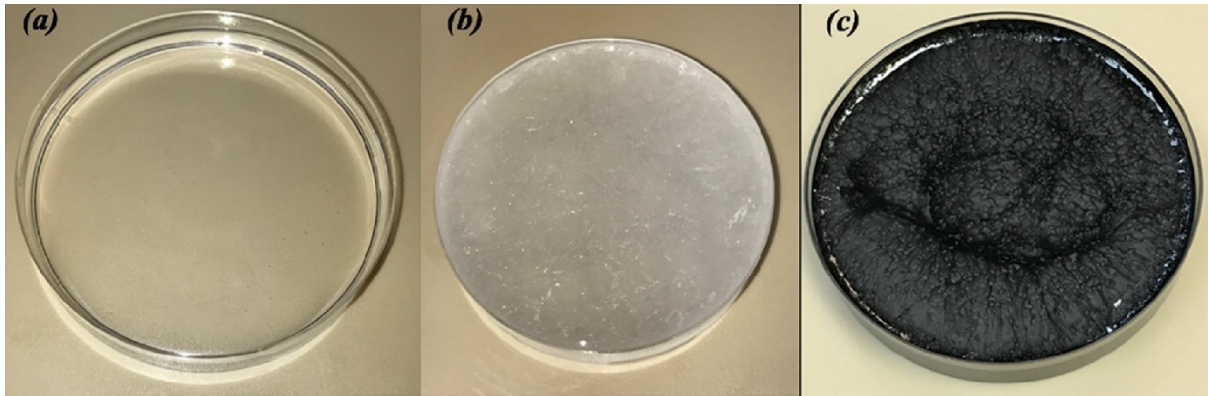


Figure 10 Images of (a) methyl palmitate and lauric acid eutectic mixture (b) form-stable gelled eutectic PCM and (c) thermally modified form-stable eutectic PCM, Figure from Saeed et al. [16]

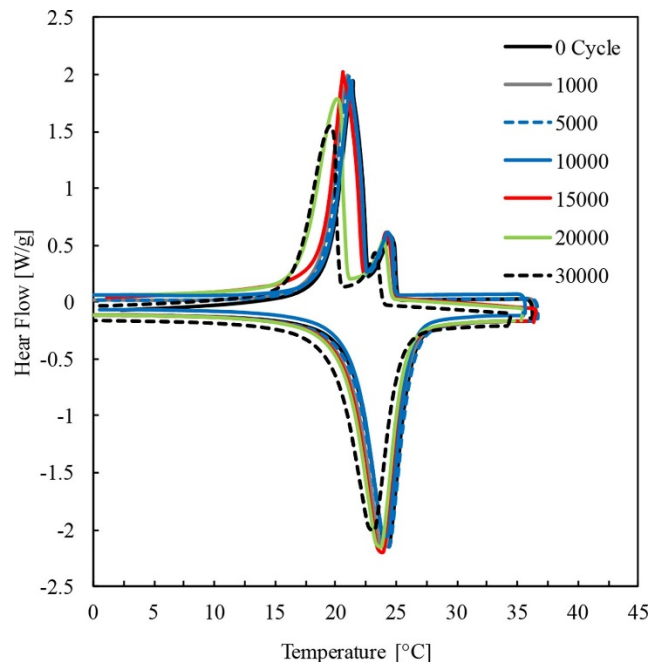


Figure 11 The DSC results of form-stable methyl palmitate and lauric acid eutectic PCM after different thermal cycling tests, Figure from Saeed et al. [16]

Agrawal et al. [63] used a thickening agent to suppress phase segregation during the curing process of the epoxy-PCM composite. The authors selected carbopol, which is a cross-linked polyacrylic acid polymer, as the thickening agent due to its known ability to stabilize and suspend pharmaceutical products. It ensures minimal phase segregation during sample synthesis. The thickening agent was added (5% in weight) into the mixture following by the other fillers and then left to cure at room temperature. Wang et al. [64] added a 1% of gellatine intending to reduce the phase segregation phenomenon of barium hydroxide octahydrate. The gellatine powders are simply mixed using a glass rod in a test tube. With the introduction of gellatine, the phase segregation phenomenon is controlled but not stopped. Wang et al. [65] also selected PAAM to prevent phase separation from the SAT based thermal storage system. The identical mass fraction of PAAM and nucleating agent (1%, 1.5% and 2%) were introduced to the melt SAT together before the mixture was stirred into a

homogenous state. Researchers indicated that with the presence of the nucleating agent, PAAm has less influence on the energy storage capacity compared to both carboxymethyl cellulose and xanthan. 1.5% of PAAm provided the best stabilization performance below 120°C. In addition, studies show that thickening/gelling agents can also cooperate with other components such as surfactant to increase the phase stability of the TES materials. Fashandi and Leung [66] selected the CMC with an average molecular weight of 250,000 as the thickener coupled with the surfactant sodium dodecyl sulphate and other additives, blended with small SAT particles ($< 53\mu\text{m}$). 3% of CMC and 0.25% of sodium dodecyl sulphate effectively inhibited the phase segregation of the composite.

From the discussion above, it is evidently that the addition of thickening/gelling agent increase the stability of the TES materials. However, adding more thickening/gelling agent does not necessarily guarantee a better performance. For instance, Wang et al. [67] studied different mass ratio of CMC in disodium hydrogen phosphate dodecahydrate composite. It shows that little CMC can be dissolved when its concentration reached 7 % in weight. Therefore the ideal working range of CMC is 0.5 - 7%. Other studies show a 3 wt.% CMC addition is enough to form a gel [68,69]. Apart from the solubility issue, the immobility of the material can be a limiting factor and bring complexity of the material filling in some cases, which is effected by the concentration and the molecular weight of the thickening/gelling agent. The addition of thickening/gelling agent also has a different degrees of negative impact on the latent heat or thermal conductivity of the materials in liquid state. The affect on supercooling on the other hand, is controversial in different studies. It is reported in Liang and Chen's research that the addition of the thickening agent reduces the driving force of crystallization by the viscosity increment [70]. Zou et al. [61] claimed that the supercooling of the thickened composite PCM increased after cycling. Wu et al.[43] compared the supercooling of the magnesium chloride solution before/after adding xanthan. It shows as a thickener, xanthan did not affect the supercooling degree. For above reasons, a proper concentration of thickening/gelling for different TES materials need to be selected. A recommended concentration range of thicken/gelling agents and other selecting criterial can be found in Table 1. Besides, the selection and the preparation of the thickening/gelling agents are less explained whilst these are essential aspects for the utilisation of the thickening/gelling agents and minimise the inconsistency of the results. Therefore a comprehensive guidance is provided as follows for the screening and formulation of thickened TES materials.

5.2 Selection of thickening/gelling agent

A selection flow chart is proposed in this section for the selection of thickening and gelling agents according to TES technologies and applications. A guidance for researchers and practitioners to perform initial thickening/gelling agent screening is provided.

As mentioned above, various of thickening/gelling agents are available on the market. To obtain the suitable candidates, several key properties such as the compatibility, operating conditions, viscosity profile, etc must be addressed. Here, a novel methodology applied to the TES field, where steps are guiding through the selection process (see Figure 12) is delivered. The first step is to evaluate the compatibility between the thickening/gelling agents and TES materials. This is done by identifying organic and inorganic agent and their intrinsic compatibility with the TES material selected. A miscible thickening/gelling agent is screened corresponding to the selected base materials, either organic or inorganic. In this step, it is important to bear in mind the goal of adding a thickening/gelling agent, e.g. increase viscosity, increasing the volume/size/percentage of the internal phase, etc. Once this has been

assessed, the operating conditions, which are defined by the TES material selected, are considered to narrow down the agent candidates. Stabilising the TES material at high or low temperatures must consider the specific gravity of the suspended material and its surface charge/modification. Besides, pH may change the effect of the agent as the pH will profoundly change the solubility and stability of the agent in the suspension. In this regard, it is important to consider the effect of the parameters at preparation temperature and at operational temperature to ensure the long-term stability of the mixture. The thickening/gelling agent candidates that meet the criteria above can be added into the TES material at different certain concentration. At this point, researchers should prepare and test the thickening/gelling agent material, exploring the minimum-maximum range of agent ratio in the TES material. The agent/ TES material should be characterised to understand its performance under operational conditions. To that end, the viscosity profile of each concentration as well as the phase temperature after cycling stability studies are measured and compared. The cycling test need to be performed subsequently to study the stability of the composite TES material before putting into application. Once the agent/ TES material is proved to work under operational conditions, the cost factor of this additive is taken into account. This is the point, where the agent candidates are assessed as the final candidates, for the agent should not highly increase the cost of the base TES material. Generally, the agents are added in sufficiently low quantities, thus cost contribution might not be an issue, however is something to consider specially for when using synthetic agents.

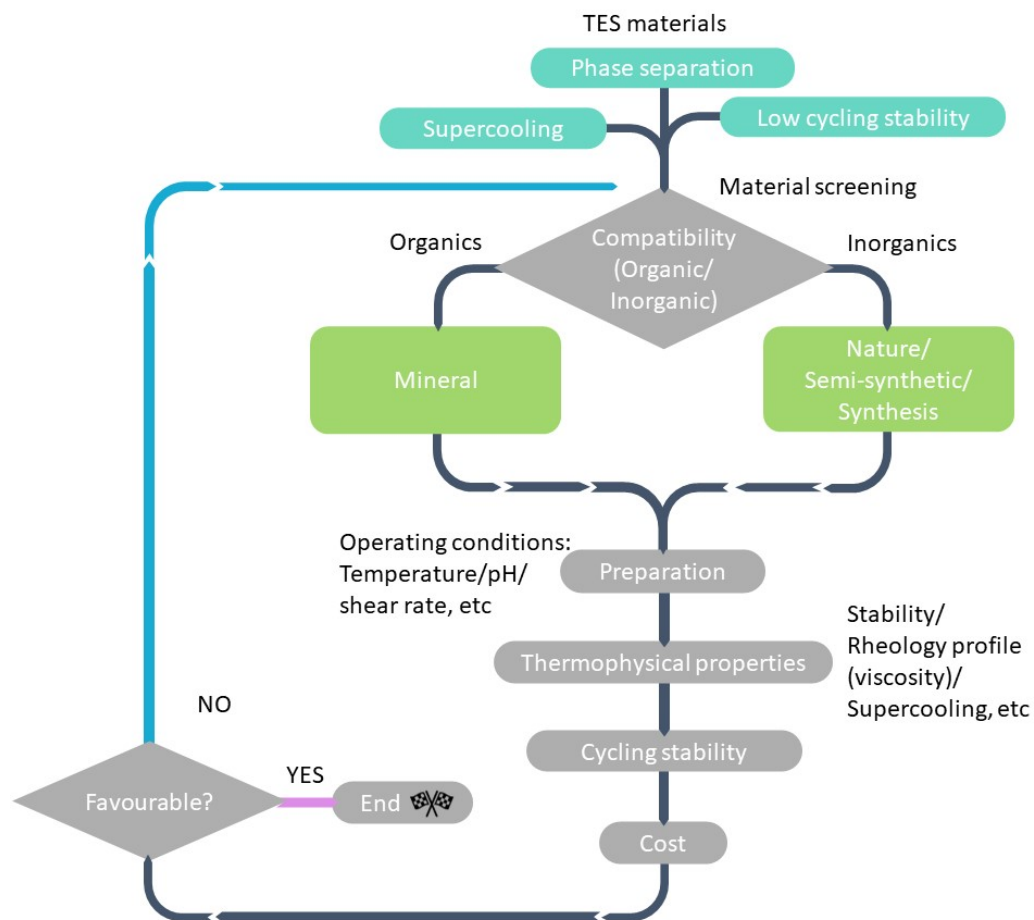


Figure 12 the thickening/gelling agents selection methodology for TES

Table 2 the properties of composites with thickening/gelling agents

Agent	Based PCM	Final thermal properties of the composites			Concentration (wt.%)	Preparation	Performance of the agent	Cycling stability	Ref.
		Latent heat (kJ/kg)	Phase change temperature (°C)	Thermal conductivity (W/m k)					
CMC	CaCl ₂ · 6H ₂ O– Ca(NO ₃) ₂ · 4H ₂ O	116 (±3%)	21.4 (Supercooling reduced ~2.2°C)	-	0.5	Mixing	Reduced supercooling	-	[71]
	CaCl ₂ · 6H ₂ O 80wt.%	127.2	11.62 (supercooling degree increased to 3.12 °C cycling)	-	2	Mixing with pre-prepared CPCM	Thickening	50 cycles	[61]
	CaCl ₂ · 6H ₂ O– MgCl ₂ · 6H ₂ O (20 wt.%)	120.62 (±1.9%)	27.39 (Supercooling degree 0.59)	-	0.5	Stir mixing	Circulation stability	100 cycles	[72]
	Mg(NO ₃) ₂ · 6H ₂ O - MgCl ₂ · 6H ₂ O (60:40)	147 (after cycling 100)	57 (after cycling 51)	-	1	Placed with pre-prepared CPCM at 80°C for 24 hours	Avoided phase segregation	100 cycles	[73]
	Mg(NO ₃) ₂ · 6H ₂ O	138 (after cycles 132.5)	87.48 (after cycles 86.95), supercooling degree decreased 20.39°C	0.807	3 (viscosity decreases above 3wt.% of CMC)	Mixing agents in the complete melted PCM for 30 mins	Thermal stability enhancement, but has minor effect on solid phase thermal conductivity	50 cycles	[74]

		227.54	52.5	-	4	Mixing with a mortar and a pestle	Thickening	50 cycles	[75]
		285.80	62.13	-	3(CMC : silica gel-85:15 mixture)	Used in along with silica gel for thickening effect	Reduced phase segregation	10 cycles	[76]
	SAT	~250 (after 5 cycles loss 2.27%)	59.5	1.85 (with 2.5 wt.% ethylene glycol)	5	Mixing agents in the complete melt PCM for 30 mins	Thickening agent reduced aggregation	5 cycles	[77]
CMC		-	-	1.1 (with 5% graphite flake)	5	-	At least 5% CMC is sufficient preventing phase segregation	-	[27]
		230-240	58-60	~1.2 (with 5 wt.% nanocomposites)	3	Dry blending	Circumvent phase segregation of salt hydrates	20 cycles	[78]
		-	58	-	3	Dry blending	Non-effective to overcome the phase segregation of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, good for low hydrates	100 cycles	[30]
	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	-	48	-	3	Dry blending		100 cycles	[30]
CMC/ nano	Encapsulated	213.3	121.2	0.84	1.5	Dispersion by	Thermal	-	[60]

Al ₂ O ₃	59.2 wt.% erythritol						ultra-turrax high speed homogenizer for 5 min, following an ultra- sonication for another 30 min.	stability enhancement		
Xanthan	SAT	205– 210	-	-	0.5		Mixed with small amount of SAT, then slowly added into melt STA	Overcome phase separation in a 1.5m reactor	40 cycles	[27]
		197.2	~58	2.1	1.5		Mixing at 75°C with melt STA	No leakage, nor deformation, good stability	200 cycles	[79]
Polyacrylamide	SAT	264	57	-	1.5		Direct mixing	Solved phase segregation problems	-	[65]
Poliviniyl alcohol (PVA)	Inorganic salt hydrates (i.e. Na ₂ CO ₃ · 10H ₂ O)	-	-	-	1-4		Direct mixing	Noneffective to sal soda	-	
acrylic acid copolymer based SAP	Na ₂ CO ₃ · 10H ₂ O		33		3-3.5			Achieved homogeneous system	150 cycles	[30]
	Na ₂ SO ₄ · 10H ₂ O		32.35	-	2.9			Effective overcome phase	300 cycles	

	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$		50			3.5		separation Eliminated phase separation	200 cycles	
	SAT					3		Non-effective for lower hydrate salts	20 cycles	
Sodium acrylate (PASS)	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	206.8	47.3	-		2	Mixed with melted PCM	Good cycling stability	100 cycles	[80]
2-HPEC	Methyl Palmitate/ Lauric Acid - 60/40 (molar ratio)	165.6	24.29	~0.34		10	Mixed with PCM mixture at 50°C for 30 min	HPEC has negative effect on thermal conductivity, positive impact on supercooling and system stability	36000 cycles	[16]
Silica with 2% Sucrose	SAT-urea non-eutectic mixture	147.8	37.81	-		30	Melt PCM mixture slowly added into SiO_2	Reduce supercooling and leaking	200 cycles	[62]
Silica	Battery electrolyte	-	-	-		30-40	Simple mixing and settling, different temperatures require different gel times	No liquid separation, high gel strength, Low concentration, small particles size are better. $\text{pH} < 2$ is better	-	[81]

Oleic acid functionalized zinc oxide nanoparticles	paraffine based mineral C15-C50 oil	-	-	0.155 for 0.1 wt.% f-ZnO-oil nanofluid at 59°C	0.1-1	Two step method and ultrasonication	Enhancing thermal conductivity, increase the viscosity of PCM	Stability increased up to 5 days	[82]
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5.3 Preparation of a thickened composite TES system

In this section the inputs on the preparation of the thickening/gelling TES material are provided. As reported in Table 2, the methods used for thickened TES composites are (1) Melting method; (2) Solution mixing method and (3) Dry blending. The mixing process can be commonly conducted with melt compounding and powder mixing. All those methods consist of three main steps illustrated in Figure 13, component weighing, mixing/stirring (either in melt or dry state) and the final homogeneous system. To formulate a thickened system, thickening/gelling agent is added into the TES materials with various of approaches. The mass ratio is needed to be optimised to meet the application requirement. Stirring improves the dispersion of the agents in the system to reach a homogeneous state. Specific conditions such as temperature, shear rate, etc. is required during this step (such as temperature activated agents, nanoparticles) to accelerate the thickening/gelling reaction. If there are other components such as thermal conductivity enhancement agent or nuclear agent in the system, in order to obtain a homogeneous system, the thickening/gelling agent is recommended to be added the last. This procedure depends strongly on the thermal property of each TES material and agent.

A brief description of each of the preparation methods reported is given below:

- (1) Melting mixing method: The melt-and-mix method refers to the mixing technique of heating (and melting) the TES material to liquid state at a specific temperature and magnetic stirring conditions (on a hot plate for instance) before combining with the dry thickening/gelling agent; followed by a mixing step with agents that can be performed with stirring, ultrasonic, etc [83].
- (2) Solution mixing method: this is a method based on a solvent system in which the TES material is soluble in the base fluid (e.g. water) and the agents are swellable in the solution. This method consists of two steps; the dissolution of the TES material (if it is soluble in water) while stirring and the addition of the agent once the material dissolved.
- (3) Dry blending: is the process of incorporating dry ingredients to produce a well-mixed dry product. The components normally have different particle size, thus sometimes the step of using a mill freezer is added into the preparation method [30], [66].

Most of the researchers use the melting mixing and the dry blending method (see Table 2) as they provide a simple approach to thickened material preparation. Some examples reported in the literature are described in the following: Ding et al. [73] introduced CMC into a well mixed composite phase change material at 80°C. The system then was held still for 24 h. Wang et al. [60] dispersed PCM and surfactant in the solvent at room temperature for 15 min. CMC or nano-Al₂O₃ were added subsequently with ultra-turrax high speed homogenizing for 5 min, which is followed by an ultra-sonication at the same temperature for another 30 min to form the emulsion. More details are listed in Section 2 and the preparation section of Table 2.

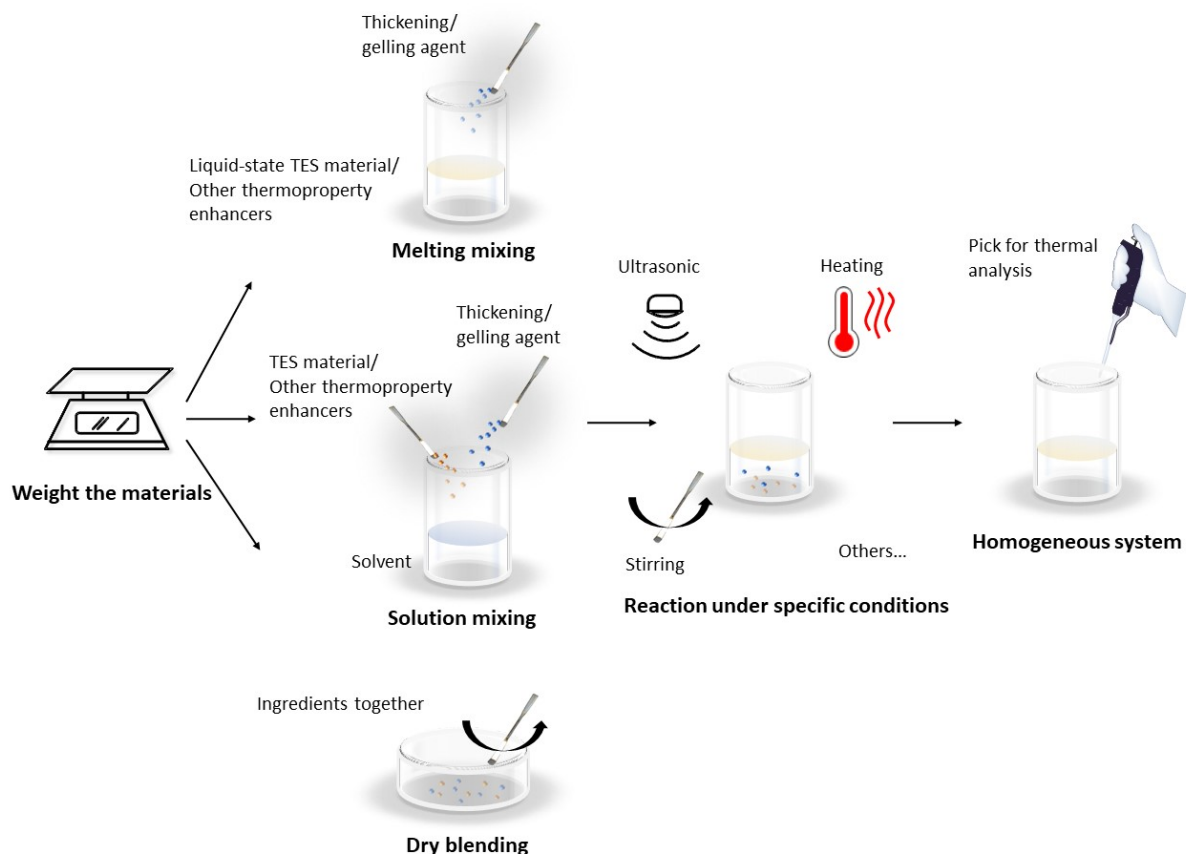


Figure 13 the schematic diagram of the preparation steps of material thickening/gelling

6. Outlook of the use of thickening and gelling agents in TES

From the number of academic publications and patents in the last 20 years, thickening/gelling is clearly on an arising trend in the TES field; see Figure 14. Both gelling and thickening are seen to be of increasing interest according to scientific publications, whereas thickening is more reported in patents than gelling.

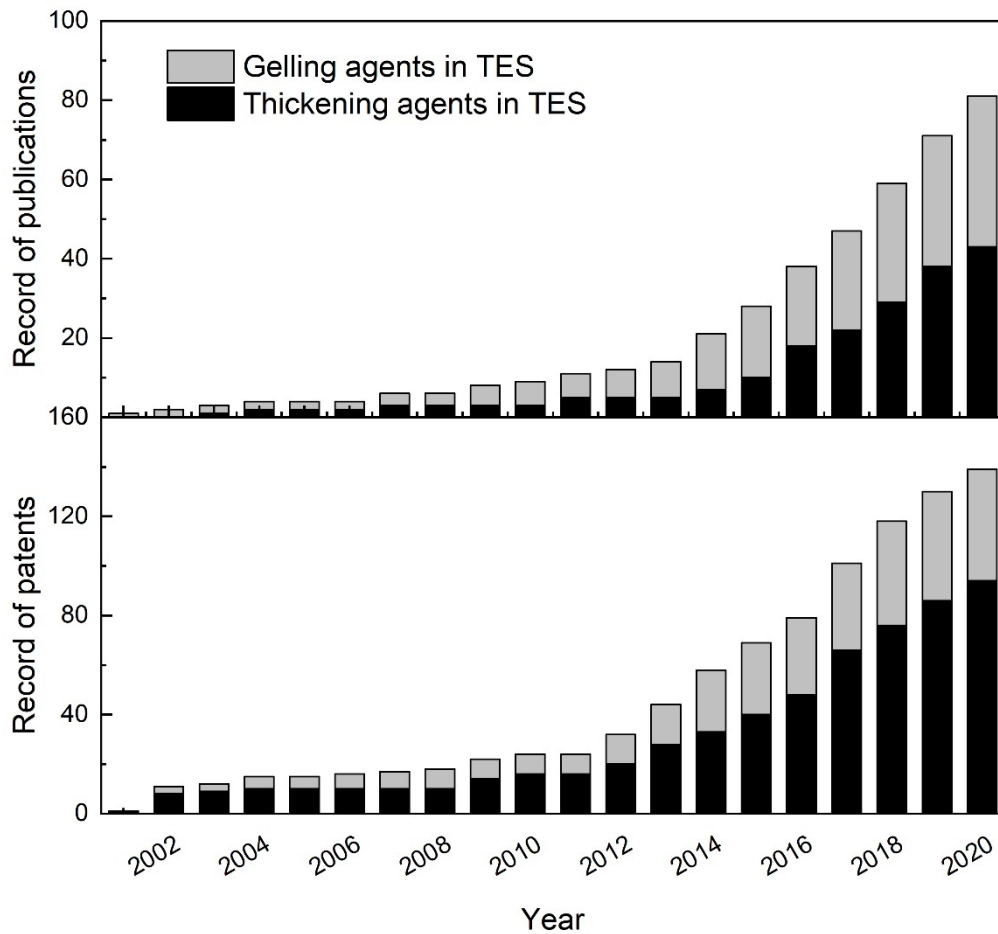


Figure 14 Publications and patents rate of thickening/gelling agents in past decades

6.1 Summary

Thickening and gelling agents that are currently used and potentially can be used in TES technologies are assessed first time in this review. The introduction of a small amounts of thickening/gelling agents (1-3% in weight) has shown to address some of the challenges in TES materials, particularly supercooling, agglomeration, and leakage (see Table 2, section 5). Also, mixing in different proportions gelling and thickening agents like guar gum, xanthan gum or locust beam with agar or CMC has been proven to increases the viscosity and firmness of PCM solutions. Figure 15 shows the overlapping of the main gelling/thickening agents cost found in the literature and the energy storage capacity of the different TES materials versus working temperature. The agents listed in this review can be chosen according to their stability over the working temperature range, agents such as carrageenan, modified starch, agar and gelatin provide a stable structure over 25-150°C. Others such as exudate gums, are indicated over a wider temperature range for medium-high temperature applications. Then, working conditions such as pH, chemical compatibility and cycling stability are important to achieve a high-performance TES material. Other relevant parameters such as cost are also considered to keep the new PCM formulation applicable.

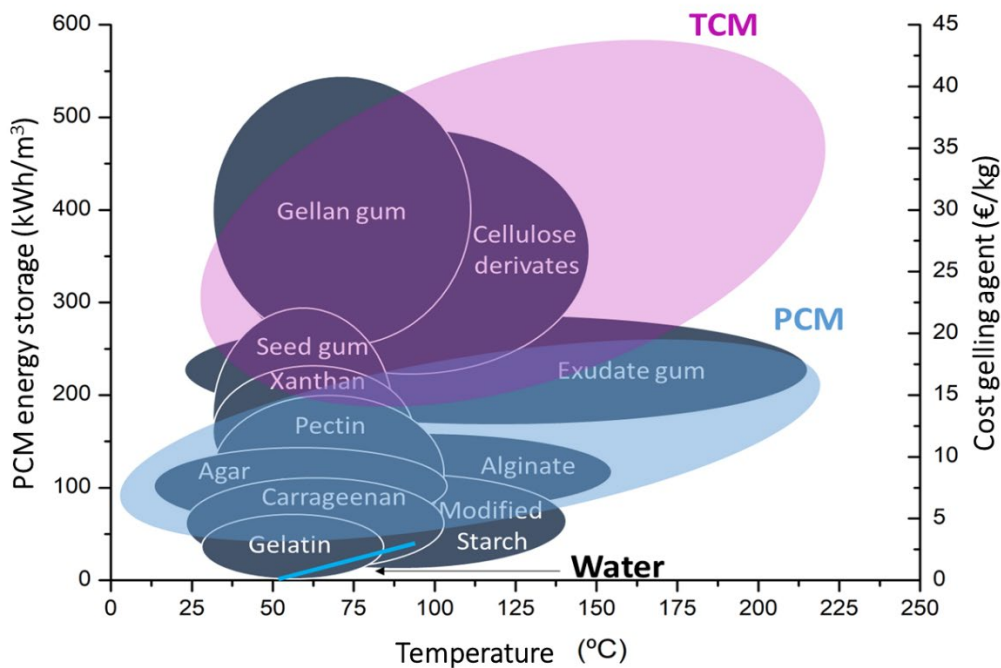


Figure 15 TES storage capacity vs thickening/gelling agent cost over the operational working range. Adapted from [84]

6.2 Challenges

The following main challenges of using thickening and gelling agents in TES can be found in this review:

Adding thickening/gelling agent sometimes can lead to a decrease in storage capacities and charge/discharge kinetics. This is one of the main challenges for thickening/gelling in TES as the energy stored is always desired to be maximised.

The preparation process of a thickened TES system can be a limiting step without guidelines mostly because of the incompatibility of thickening/gelling agents and TES materials: some thickening agents require dissolution in water while some TES materials do not dissolve in water; some thickening agents require heat to be involved, which can change the initial state of the storage material (e.g. salt hydrates).

Among all the additives commercially available (see Section 2), only a few have been explored in TES filed. As described in Section 5.1, most of the studies use CMC mainly to prevent phase segregation and supercooling. However, it can not meet the diverse of requirements regarding the viscosity profile and material compatibility.

6.3 Future work

Introducing thickening and gelling agents in TES materials is a promising way for the immobilisation and shape stabilisation yet few studies have been conducted in this field. A proper thickening and gelling agent screening for the different TES materials should be performed to provide an experimental validation of the properties and the interactions between agents and TES materials. The preparation method should be discussed as most of

the publications report a simple method without critical details, for instance, the preparation condition or the properties of the solution. Another task that remains pending is to explore novel, cost-wise competitive alternatives of gelling/thickening agents that is feasible in the working temperature range and stable conditions. One objective of this review can raise more interest of researchers of this field and to inspire more studies.

Acknowledgements

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References

- [1] Lochhead RY. The Use of Polymers in Cosmetic Products. *Cosmet. Sci. Technol. Theor. Princ. Appl.*, Elsevier Inc.; 2017, p. 171–221. <https://doi.org/10.1016/B978-0-12-802005-0.00013-6>.
- [2] Dull-Muhlbach I. Unsaturated polyester and vinyl ester resins. *Kunststoffe, Ger Plast* 1993;83:55–8. <https://doi.org/10.1016/b978-081551421-3.50007-2>.
- [3] Kulkarni VS, Shaw C. Introduction. *Essent. Chem. Formul. Semisolid Liq. Dosages*, Elsevier; 2016, p. 1–4. <https://doi.org/10.1016/b978-0-12-801024-2.00001-7>.
- [4] Saha D, Bhattacharya S. Hydrocolloids as thickening and gelling agents in food: A critical review. *J Food Sci Technol* 2010;47:587–97. <https://doi.org/10.1007/s13197-010-0162-6>.
- [5] Karsheva M, Georgieva S, Handjieva S. the Choice of the Thickener - a Way To Improve the Cosmetics Sensory Properties. *J Univ Chem Technol Metall* 2007;42:187–94.
- [6] Fink JK. *Fracturing Fluids. Pet. Eng. Guid. to Oil F. Chem. Fluids*, Elsevier; 2012, p. 519–83. <https://doi.org/10.1016/b978-0-12-383844-5.00017-9>.
- [7] Cabeza LF, Castell A, Barreneche C, De Gracia A, Fernández AI. Materials used as PCM in thermal energy storage in buildings: A review. *Renew Sustain Energy Rev* 2011;15:1675–95. <https://doi.org/10.1016/j.rser.2010.11.018>.
- [8] Fallahi A, Guldentops G, Tao M, Granados-Focil S, Van Dessel S. Review on solid-solid phase change materials for thermal energy storage: Molecular structure and thermal properties. *Appl Therm Eng* 2017;127:1427–41. <https://doi.org/10.1016/j.applthermaleng.2017.08.161>.
- [9] Raj CR, Suresh S, Bhavsar RR, Singh VK. Recent developments in thermo-physical property enhancement and applications of solid solid phase change materials: A review. *J Therm Anal Calorim* 2020. <https://doi.org/10.1007/s10973-019-08703-w>.
- [10] Beaupere N, Soupremanien U, Zalewski L. Nucleation triggering methods in supercooled phase change materials (PCM), a review. *Thermochim Acta* 2018;670:184–201. <https://doi.org/10.1016/j.tca.2018.10.009>.
- [11] Oró E, de Gracia A, Castell A, Farid MM, Cabeza LF. Review on phase change materials (PCMs) for cold thermal energy storage applications. *Appl Energy* 2012;99:513–33. <https://doi.org/10.1016/j.apenergy.2012.03.058>.
- [12] Farid MM, Khudhair AM, Razack SAK, Al-Hallaj S. A review on phase change energy storage: materials and applications. *Energy Convers Manag* 2004;45:1597–615. <https://doi.org/10.1016/j.enconman.2003.09.015>.
- [13] Wong-Pinto LS, Milian Y, Ushak S. Progress on use of nanoparticles in salt hydrates as phase change materials. *Renew Sustain Energy Rev* 2020;122:109727. <https://doi.org/10.1016/j.rser.2020.109727>.
- [14] Beaupere N, Soupremanien U, Zalewski L. Nucleation triggering methods in supercooled phase change materials (PCM), a review. *Thermochim Acta* 2018;670:184–201. <https://doi.org/10.1016/j.tca.2018.10.009>.
- [15] Kenisarin M, Mahkamov K. Salt hydrates as latent heat storage materials: Thermophysical properties and costs. *Sol Energy Mater Sol Cells* 2016;145:255–86. <https://doi.org/10.1016/j.solmat.2015.10.029>.

- [16] Saeed RM, Schlegel JP, Castano C, Sawafta R. Preparation and enhanced thermal performance of novel (solid to gel) form-stable eutectic PCM modified by nano-graphene platelets. *J Energy Storage* 2018;15:91–102. <https://doi.org/10.1016/j.est.2017.11.003>.
- [17] Hua W, Zhang X, Muthoka MJ, Han X. Preparation and performance analysis of modified sodium acetate trihydrate. *Materials (Basel)* 2018;11. <https://doi.org/10.3390/ma11061016>.
- [18] Mudgil D, Barak S, Khatkar BS. Guar gum: Processing, properties and food applications - A Review. *J Food Sci Technol* 2014;51:409–18. <https://doi.org/10.1007/s13197-011-0522-x>.
- [19] Abbas KA, K. Khalil S, Meor Hussin AS. Modified Starches and Their Usages in Selected Food Products: A Review Study. *J Agric Sci* 2010;2. <https://doi.org/10.5539/jas.v2n2p90>.
- [20] Kulkarni VS, Shaw C. Formulating Creams, Gels, Lotions, and Suspensions. *Essent. Chem. Formul. Semisolid Liq. Dosages*, Elsevier; 2016, p. 29–41. <https://doi.org/10.1016/b978-0-12-801024-2.00004-2>.
- [21] Kadajji VG, Betageri G V. Water soluble polymers for pharmaceutical applications. *Polymers (Basel)* 2011;3:1972–2009. <https://doi.org/10.3390/polym3041972>.
- [22] Wüstenberg T. General Overview of Food Hydrocolloids. *Cellul. Cellul. Deriv. Food Ind.*, 2014, p. 1–68. <https://doi.org/10.1002/9783527682935.ch01>.
- [23] Armisen R, Fox JE, Gerrish TC, Gibson W, Humphreys W, Imeson AP, et al. *Thickening and Gelling Agents for Food*. 1997.
- [24] Imeson A. Food stabilisers, thickeners and gelling agents. 2010. <https://doi.org/10.1192/bjp.112.483.211-a>.
- [25] Wang HMD, Chen CC, Huynh P, Chang JS. Exploring the potential of using algae in cosmetics. *Bioresour Technol* 2015;184:355–62. <https://doi.org/10.1016/j.biortech.2014.12.001>.
- [26] Fu S, Thacker A, Sperger DM, Boni RL, Velankar S, Munson EJ, et al. Rheological evaluation of inter-grade and inter-batch variability of sodium alginate. *AAPS PharmSciTech* 2010;11:1662–74. <https://doi.org/10.1208/s12249-010-9547-0>.
- [27] Dannemand M, Johansen JB, Furbo S. Solidification behavior and thermal conductivity of bulk sodium acetate trihydrate composites with thickening agents and graphite. *Sol Energy Mater Sol Cells* 2016;145:287–95. <https://doi.org/10.1016/j.solmat.2015.10.038>.
- [28] Oró E, Miró L, Barreneche C, Martorell I, Farid MM, Cabeza LF. Corrosion of metal and polymer containers for use in PCM cold storage. *Appl Energy* 2013;109:449–53. <https://doi.org/10.1016/j.apenergy.2012.10.049>.
- [29] He Y, Zhang N, Yuan Y, Cao X, Sun L, Song Y. Improvement of supercooling and thermal conductivity of the sodium acetate trihydrate for thermal energy storage with α -Fe₂O₃ as additive. *J Therm Anal Calorim* 2018;133:859–67. <https://doi.org/10.1007/s10973-018-7166-2>.
- [30] Ryu HW, Woo SW, Shin BC, Kim SD. Prevention of supercooling and stabilization of inorganic salt hydrates as latent heat storage materials. *Sol Energy Mater Sol Cells* 1992;27:161–72. [https://doi.org/10.1016/0927-0248\(92\)90117-8](https://doi.org/10.1016/0927-0248(92)90117-8).

- [31] Harvesting S, Processin S. in Food Manufacturing. 2016. <https://doi.org/10.1016/B978-0-12-811449-0/00006-2>.
- [32] Nordqvist D, Vilgis TA. Rheological Study of the Gelation Process of Agarose-Based Solutions. *Food Biophys* 2011;6:450–60. <https://doi.org/10.1007/s11483-011-9225-0>.
- [33] Cichero JAY. Thickening agents used for dysphagia management: Effect on bioavailability of water, medication and feelings of satiety. *Nutr J* 2013;12:1–8. <https://doi.org/10.1186/1475-2891-12-54>.
- [34] Bosscher D, Van Caillie-Bertrand M, Deelstra H. Do thickening properties of locust bean gum affect the amount of calcium, iron and zinc available for absorption from infant formula? In vitro studies. *Int J Food Sci Nutr* 2003;54:261–8. <https://doi.org/10.1080/09637480120092080>.
- [35] Efimova A, Pinnau S, Mischke M, Breitkopf C, Ruck M, Schmidt P. Development of salt hydrate eutectics as latent heat storage for air conditioning and cooling. *Thermochim Acta* 2014;575:276–8. <https://doi.org/10.1016/j.tca.2013.11.011>.
- [36] Larsen CK, Gåserød O, Smidsrød O. A novel method for measuring hydration and dissolution kinetics of alginate powders. *Carbohydr Polym* 2003;51:125–34. [https://doi.org/10.1016/S0144-8617\(02\)00139-X](https://doi.org/10.1016/S0144-8617(02)00139-X).
- [37] Yang L, Villalobos U, Akhmetov B, Gil A, Khor JO, Palacios A, et al. A comprehensive review on sub-zero temperature cold thermal energy storage materials, technologies, and applications: State of the art and recent developments. *Appl Energy* 2021;288:116555. <https://doi.org/10.1016/j.apenergy.2021.116555>.
- [38] Dong X, Mao J, Geng S, Li Y, Hou P, Lian H. Study on performance optimization of sodium sulfate decahydrate phase change energy storage materials. *J Therm Anal Calorim* 2021;143:3923–34. <https://doi.org/10.1007/s10973-020-09306-6>.
- [39] Das N, Triparthi N, Basu S, Bose C, Maitra S, Khurana S. Progress in the development of gelling agents for improved culturability of microorganisms. *Front Microbiol* 2015;6:1–7. <https://doi.org/10.3389/fmicb.2015.00698>.
- [40] Kulkarni VS, Shaw C. Use of Polymers and Thickeners in Semisolid and Liquid Formulations. *Essent. Chem. Formul. Semisolid Liq. Dosages*, 2016. <https://doi.org/10.1016/b978-0-12-801024-2.00005-4>.
- [41] El Karsani KSM, Al-Muntasher GA, Sultan AS, Hussein IA. Impact of salts on polyacrylamide hydrolysis and gelation: New insights. *J Appl Polym Sci* 2014;131:n/a-n/a. <https://doi.org/10.1002/app.41185>.
- [42] Maurya NK, Mandal A. Studies on behavior of suspension of silica nanoparticle in aqueous polyacrylamide solution for application in enhanced oil recovery. *Pet Sci Technol* 2016;34:429–36. <https://doi.org/10.1080/10916466.2016.1145693>.
- [43] Wu T, Xie N, Niu J, Luo J, Gao X, fang Y, et al. Preparation of a low-temperature nanofluid phase change material: MgCl₂–H₂O eutectic salt solution system with multi-walled carbon nanotubes (MWCNTs). *Int J Refrig* 2020;113:136–44. <https://doi.org/10.1016/j.ijrefrig.2020.02.008>.
- [44] Richard G. Jones, Jaroslav Kahovec, Robert Stepto, Edward S. Wilks Michael Hess, Tatsuki Kitayama WVM. *Compendium of Polymer Terminology and Nomenclature*. 2018.
- [45] Maitra J, Kumar Shukla V. Cross-linking in Hydrogels-A Review. *Am J Polym Sci*

- 2014;2014:25–31. <https://doi.org/10.5923/j.ajps.20140402.01>.
- [46] Redaelli F, Sorbona M, Rossi F. Synthesis and processing of hydrogels for medical applications. *Bioresorbable Polym. Biomed. Appl. From Fundam. to Transl. Med.*, Elsevier; 2017, p. 205–28. <https://doi.org/10.1016/B978-0-08-100262-9.00010-0>.
- [47] TEGO® ViscoPlus. Rheological Additives - Technical background. n.d.
- [48] Tako M, Tamaki Y, Teruya T, Takeda Y. The Principles of Starch Gelatinization and Retrogradation. *Food Nutr Sci* 2014;05:280–91. <https://doi.org/10.4236/fns.2014.53035>.
- [49] Timilsena YP, Akanbi TO, Khalid N, Adhikari B, Barrow CJ. Complex coacervation: Principles, mechanisms and applications in microencapsulation. *Int J Biol Macromol* 2019;121:1276–86. <https://doi.org/10.1016/j.ijbiomac.2018.10.144>.
- [50] Gopinathan J, Noh I. Click Chemistry-Based Injectable Hydrogels and Bioprinting Inks for Tissue Engineering Applications. *Tissue Eng Regen Med* 2018;15:531–46. <https://doi.org/10.1007/s13770-018-0152-8>.
- [51] Xu J, Liu Y, Hsu S hui. Hydrogels based on schiff base linkages for biomedical applications. *Molecules* 2019;24:1–21. <https://doi.org/10.3390/molecules24163005>.
- [52] Zhao H. State-of-the-art of standing supports for gob-side entry retaining technology in China. *J South African Inst Min Metall* 2019;119:891–906. <https://doi.org/10.17159/2411-9717/17/449/2019>.
- [53] Song K, Kim Y, Chang G. Rheology of Concentrated Xanthan Gum Solutions : Steady Shear Flow Behavior 2006;7:129–38.
- [54] University-geneva C, Ny G. COMPLEX VISCOSITY-TEMPERATURE MASTER CURVE OF CORNSTARCH DISPERSION DURING GELATINIZATION 1998;21:191–207.
- [55] Kök MS, Hill SE, Mitchell JR. Viscosity of galactomannans during high temperature processing: Influence of degradation and solubilisation. *Food Hydrocoll* 1999;13:535–42. [https://doi.org/10.1016/S0268-005X\(99\)00040-5](https://doi.org/10.1016/S0268-005X(99)00040-5).
- [56] Efimova A, Pinnau S, Mischke M, Breitkopf C, Ruck M, Schmidt P. Development of salt hydrate eutectics as latent heat storage for air conditioning and cooling. *Thermochim Acta* 2014;575:276–8. <https://doi.org/10.1016/j.tca.2013.11.011>.
- [57] Xiao Q, Zhang M, Fan J, Li L, Xu T, Yuan W. Thermal conductivity enhancement of hydrated salt phase change materials employing copper foam as the supporting material. *Sol Energy Mater Sol Cells* 2019;199:91–8. <https://doi.org/10.1016/J.SOLMAT.2019.04.020>.
- [58] Dannemand M, Dragsted J, Fan J, Johansen JB, Kong W, Furbo S. Experimental investigations on prototype heat storage units utilizing stable supercooling of sodium acetate trihydrate mixtures. *Appl Energy* 2016;169:72–80. <https://doi.org/10.1016/j.apenergy.2016.02.038>.
- [59] Li X, Zhou Y, Nian H, Zhu F, Ren X, Dong O, et al. Preparation and thermal energy storage studies of CH₃COONa·3H₂O-KCl composites salt system with enhanced phase change performance. *Appl Therm Eng* 2016;102:708–15. <https://doi.org/10.1016/j.applthermaleng.2016.04.029>.
- [60] Wang Y, Li S, Zhang T, Zhang D, Ji H. Supercooling suppression and thermal behavior improvement of erythritol as phase change material for thermal energy

- storage. *Sol Energy Mater Sol Cells* 2017;171:60–71. <https://doi.org/10.1016/j.solmat.2017.06.027>.
- [61] Zou T, Fu W, Liang X, Wang S, Gao X, Zhang Z, et al. Preparation and performance of modified calcium chloride hexahydrate composite phase change material for air-conditioning cold storage. *Int J Refrig* 2018;95:175–81. <https://doi.org/10.1016/j.ijrefrig.2018.08.001>.
- [62] Fu W, Zou T, Liang X, Wang S, Gao X, Zhang Z, et al. Preparation and properties of phase change temperature-tuned composite phase change material based on sodium acetate trihydrate–urea/fumed silica for radiant floor heating system. *Appl Therm Eng* 2019;162:114253. <https://doi.org/10.1016/J.APPLTHERMALENG.2019.114253>.
- [63] Agrawal R, Joshua Hanna, Emre Gunduz I, Luhrs CC. Epoxy–PCM composites with nanocarbons or multidimensional boron nitride as heat flow enhancers. *Molecules* 2019;24. <https://doi.org/10.3390/molecules24101883>.
- [64] Wang Q, Wang J, Chen Y, Zhao CY. Experimental investigation of barium hydroxide octahydrate as latent heat storage materials. *Sol Energy* 2019;177:99–107. <https://doi.org/10.1016/j.solener.2018.11.013>.
- [65] Wang Y, Yu K, Peng H, Ling X. Preparation and thermal properties of sodium acetate trihydrate as a novel phase change material for energy storage. *Energy* 2019;167:269–74. <https://doi.org/10.1016/j.energy.2018.10.164>.
- [66] Fashandi M, Leung SN. Sodium acetate trihydrate-chitin nanowhisker nanocomposites with enhanced phase change performance for thermal energy storage. *Sol Energy Mater Sol Cells* 2018. <https://doi.org/10.1016/j.solmat.2018.01.037>.
- [67] Wang Z, Yang L, Hu J, Hu X, Gu Z. Experimental Study on Phase Change Thermal Storage of Crystalline Hydrated Salt Applied in Solar Thermal Utilization. *Procedia Eng* 2017;205:2259–65. <https://doi.org/10.1016/j.proeng.2017.10.071>.
- [68] Ghannam MT, Esmail MN. Rheological properties of carboxymethyl cellulose. *J Appl Polym Sci* 1997. [https://doi.org/10.1002/\(sici\)1097-4628\(19970411\)64:2<289::aid-app9>3.0.co;2-n](https://doi.org/10.1002/(sici)1097-4628(19970411)64:2<289::aid-app9>3.0.co;2-n).
- [69] Kästner U, Hoffmann H, Dönges R, Hilbig J. Structure and solution properties of sodium carboxymethyl cellulose. *Colloids Surfaces A Physicochem Eng Asp* 1997. [https://doi.org/10.1016/S0927-7757\(96\)03786-7](https://doi.org/10.1016/S0927-7757(96)03786-7).
- [70] Liang L, Chen X. Preparation and Thermal Properties of Eutectic Hydrate Salt Phase Change Thermal Energy Storage Material. *Int J Photoenergy* 2018;2018. <https://doi.org/10.1155/2018/6432047>.
- [71] Zhu FY, Zhou HX, Zhou YQ, Ge HW, Fang WC, Fang Y, et al. Phase change performance assessment of salt mixtures for thermal energy storage material. *Int J Energy Res* 2017;41:1855–66. <https://doi.org/10.1002/er.3747>.
- [72] He M, Yang L, Zhang Z. Experimental studies on cycling stable characteristics of inorganic phase change material $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ - $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ modified with $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and CMC. *IOP Conf Ser Earth Environ Sci* 2018;108:022058. <https://doi.org/10.1088/1755-1315/108/2/022058>.
- [73] Ding Q, Luo X, Lin X, Zhang H. Study of magnesium nitrate hexahydrate and magnesium chloride hexahydrate mixture as phase change material. *Asia-Pacific Power Energy Eng Conf APPEEC* 2012:1–4.

<https://doi.org/10.1109/APPEEC.2012.6306921>.

- [74] Wang H, Guo L, Liu K, Song Z, Wu L, Fang M, et al. Investigation of magnesium nitrate hexahydrate based phase change materials containing nanoparticles for thermal energy storage. *Mater Res Express* 2019;6:105512. <https://doi.org/10.1088/2053-1591/ab386f>.
- [75] Hu P, Lu DJ, Fan XY, Zhou X, Chen ZS. Phase change performance of sodium acetate trihydrate with AlN nanoparticles and CMC. *Sol Energy Mater Sol Cells* 2011;95:2645–9. <https://doi.org/10.1016/j.solmat.2011.05.025>.
- [76] Garay Ramirez BML, Glorieux C, Martin Martinez ES, Flores Cuautle JJA. Tuning of thermal properties of sodium acetate trihydrate by blending with polymer and silver nanoparticles. *Appl Therm Eng* 2014;62:838–44. <https://doi.org/10.1016/j.applthermaleng.2013.09.049>.
- [77] Shin HK, Park M, Kim HY, Park SJ. Thermal property and latent heat energy storage behavior of sodium acetate trihydrate composites containing expanded graphite and carboxymethyl cellulose for phase change materials. *Appl Therm Eng* 2015;75:978–83. <https://doi.org/10.1016/j.applthermaleng.2014.10.035>.
- [78] Fashandi M, Leung SN. Sodium acetate trihydrate-chitin nanowhisiker nanocomposites with enhanced phase change performance for thermal energy storage. *Sol Energy Mater Sol Cells* 2018;178:259–65. <https://doi.org/10.1016/j.solmat.2018.01.037>.
- [79] Xiao Q, Zhang M, Fan J, Li L, Xu T, Yuan W. Thermal conductivity enhancement of hydrated salt phase change materials employing copper foam as the supporting material. *Sol Energy Mater Sol Cells* 2019;199:91–8. <https://doi.org/10.1016/J.SOLMAT.2019.04.020>.
- [80] Zhang Y, Zhang X, Xu X, Munyalo JM, Liu L, Liu X, et al. Preparation and characterization of sodium sulfate pentahydrate/sodium pyrophosphate composite phase change energy storage materials. *J Mol Liq* 2019;280:360–6. <https://doi.org/10.1016/j.molliq.2019.01.127>.
- [81] Lambert DWH, Greenwood PHJ, Reed MC. Advances in gelled-electrolyte technology for valve-regulated lead-acid batteries. *J Power Sources* 2002;107:173–9. [https://doi.org/10.1016/S0378-7753\(01\)01072-2](https://doi.org/10.1016/S0378-7753(01)01072-2).
- [82] Ilyas SU, Narahari M, Theng JTY, Pendyala R. Experimental evaluation of dispersion behavior, rheology and thermal analysis of functionalized zinc oxide-paraffin oil nanofluids. *J Mol Liq* 2019;294:111613. <https://doi.org/10.1016/j.molliq.2019.111613>.
- [83] Ilyas SU, Narahari M, Theng JTY, Pendyala R. Experimental evaluation of dispersion behavior, rheology and thermal analysis of functionalized zinc oxide-paraffin oil nanofluids. *J Mol Liq* 2019. <https://doi.org/10.1016/j.molliq.2019.111613>.
- [84] Laevemann E. *Energiespeicher Thermische. Theoretische Grenzen und Beurteilungskriterien. Potentiale und Grenzen der Steig. der Energiespeicherdichten*, Berlin, Germany: 2010.

