Application of Nanocellulose-based Composites in Salt Hydrate Phase Change Materials for Thermal Energy Storage

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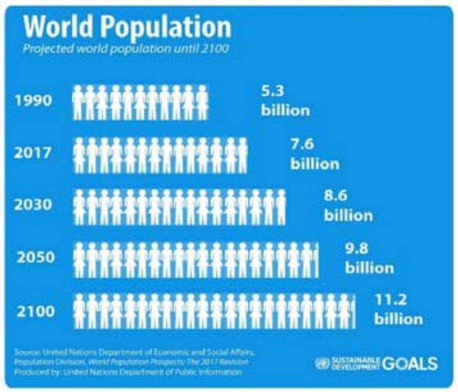
TAPPI Nano 2021 Virtual Conference

15-16 June 2021

1. Introduction

Energy crisis & renewable energies



Ever-increasing world population (Source: UN)

Growing economy and industries

Wind energy

Overconsumption of fossil energy resources

Concern about the energy crisis

Solar energy

Thermal energy storage (TES)

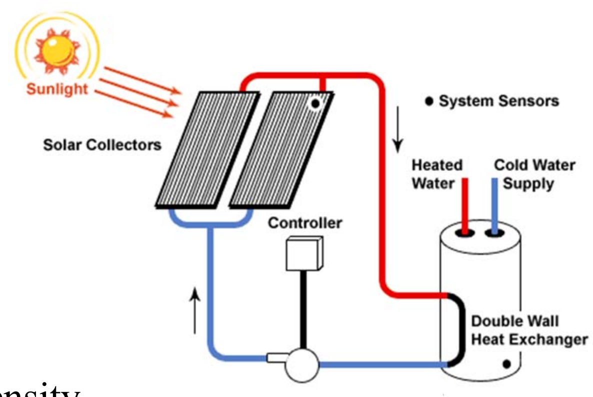
- Easy operation, low investment, good environmental impact…

Sensible heat storage (SHS):

- Energy storage through the temperature changes of materials

Cons of SHS

- Heat loss problems
- Low heat storage density
- Poor efficiency



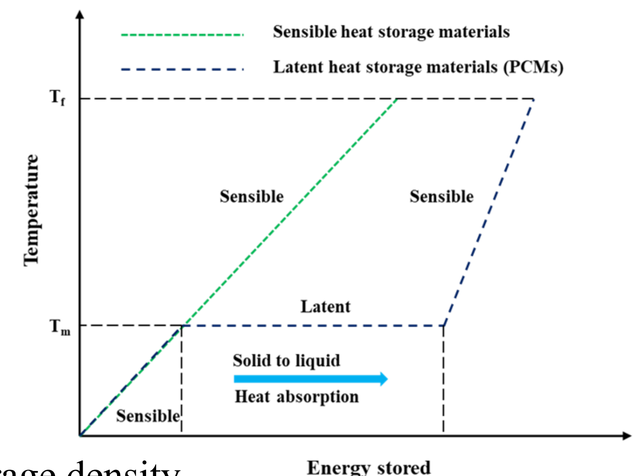
Solar water system

Latent heat storage (LHS):

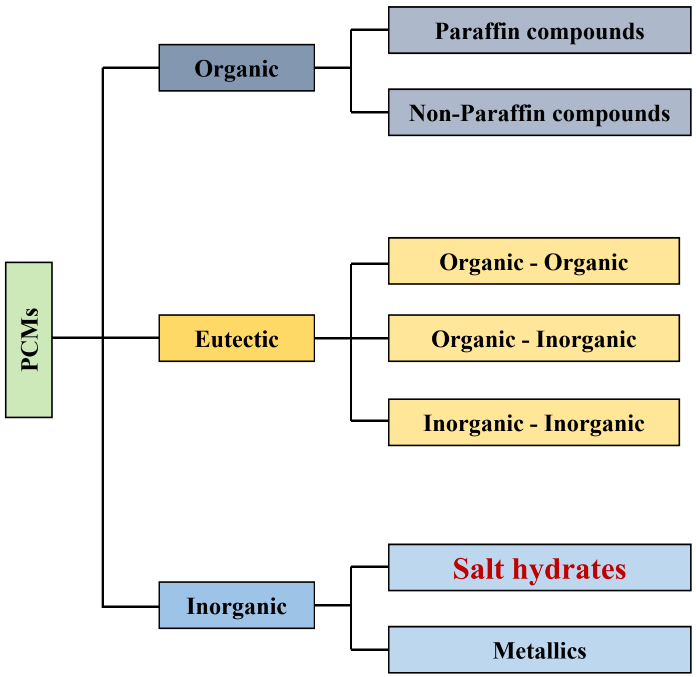
- Energy storage via **phase transitions** of materials
- Phase changes materials (PCMs)

Pros of LHS

- High efficiency
- High energy storage density
- Small temperature swings



Phase change materials (PCMs)



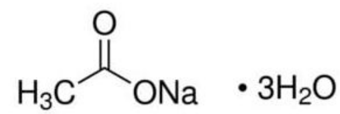
Salt hydrates

- $AB \cdot nH_2O$: alloys of inorganic salts and water
- $AB \cdot nH_2O \rightarrow AB + nH_2O$ ➡ melting (dehydration)
- $AB + nH_2O \rightarrow AB \cdot nH_2O$ ➡ freezing (hydration)

Sodium acetate trihydrate (SAT) for TES

Basic properties

- Phase change temperature: 58 °C
- Latent heat of fusion: 264 kJ/kg
- k: 0.4-0.7 W/(m·K)



Structure of SAT

Disadvantages of SAT

- Phase separation
- Supercooling

Applications

- Space heating
- Hot water supplying
- Industrial waste heat recovery

Appearance of SAT

- Dannemand, M., et al. (2016). Solar Energy Materials and Solar Cells, 145, 287-295.
- Hu, P., et al. (2011). Solar Energy Materials and Solar Cells, 95(9), 2645-2649.

※ Phase separation

Causes

- ➢ Incongruent melting
- ➢ Higher density than water

Salt hydrate

Source of image:
Wang, Y., et al. (2019). Energy, 167, 269-274.

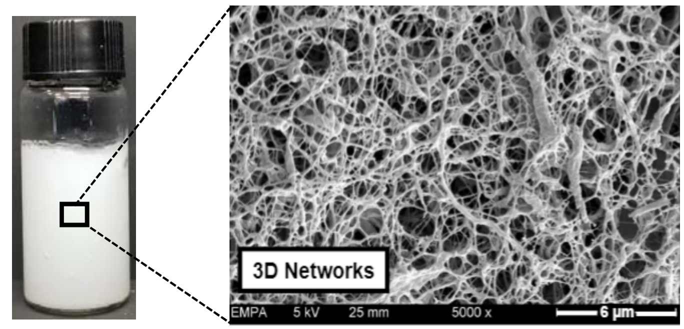
Influences

- Worse reformation of salt crystals
- Reduced heat storage capacity
- Decreased reliability of PCMs

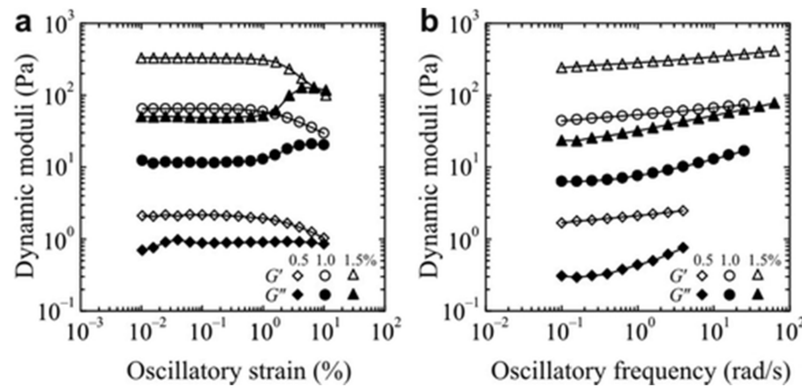
Solutions

✓ Thickeners: CMC, gelatin, polyacrylamide …

3D network of cellulose nanofibril (CNF)



CNF **CNF networks**



Rheology properties of CNF suspensions at different consistencies (0.5–1.5 wt %)

- Dannemand, M., et al. (2015). Appl. Therm. Eng., 91, 671-678.
- Nechyporchuk, O., et al. (2015). Cellulose, 22(4), 2197-2210.
- Pääkkö, M., et al. (2007) Biomacromolecules, 8(6): p. 1934-1941.
- Dimic-Misic, K., et al. (2013) Cellulose, 20(6): p. 2847-2861.
- Nechyporchuk, O., et al. (2014) Carbohydr polym, 112: p. 432-439.

※ Supercooling

Causes

- ➢ Lack of nuclei for crystallization

Supercooled liquid (left) and crystalized liquid (right)

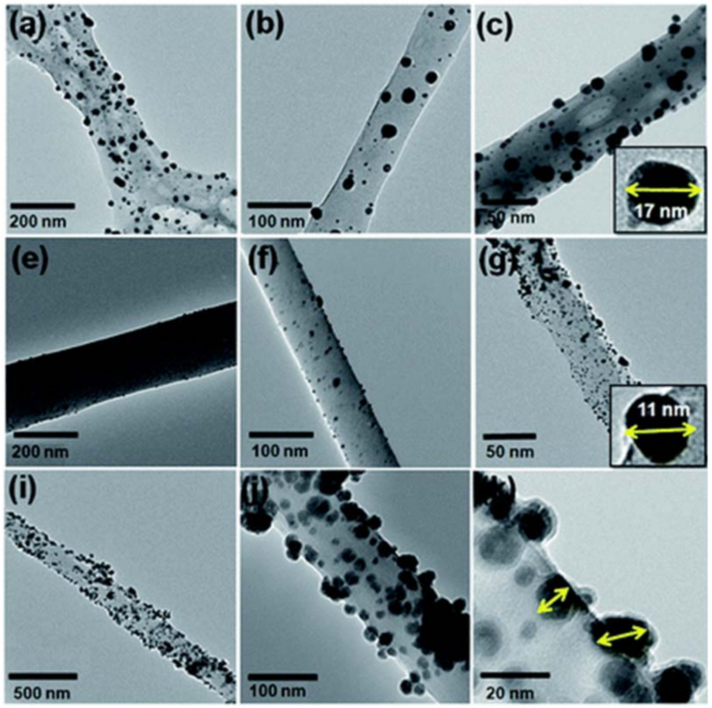
Influences

- Reduced crystallization temperature
- Large temperature difference between energy storage and release
- Less efficient energy storage and release

Solutions

✓ Addition of nucleating agents: e.g. salt hydrates, ***nanoparticles***…

CNF as support and stabilizer for NPs



TEM images of CNF/Ag (a-c), CNF/Au (e-g) and CNF/Ni (i–k)

- Dannemand, M., et al. (2015). Applied Thermal Engineering, 91, 671-678.
- Safari, A., et al. (2017). Renewable and Sustainable Energy Reviews, 70, 905-919.
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※ Thermal conductivity

- Ability to conduct heat, κ
- A low κ limits the efficient transmission of heat flow
- An improved κ accelerates heat absorption and release

Ways to improve κ

- Metal-based materials
- **Carbon nanomaterials**
  - excellent heat transfer performance
- Others…

- Sengupta R, et al. Progress in Polymer Science, 2011. 36(5): p. 638-670.
- Balandin AA, et al. Nano letters, 2008. 8(3): p. 902-907.
- Yang Y, et al. Molecules, 2019. 24(6).
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- Han, Z., & Fina, A. (2011). Progress in polymer science, 36(7), 914-944.
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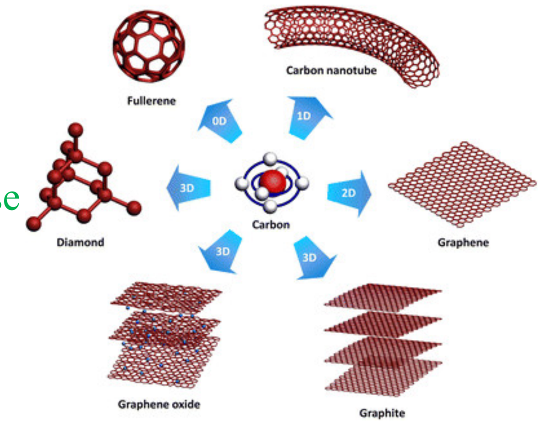
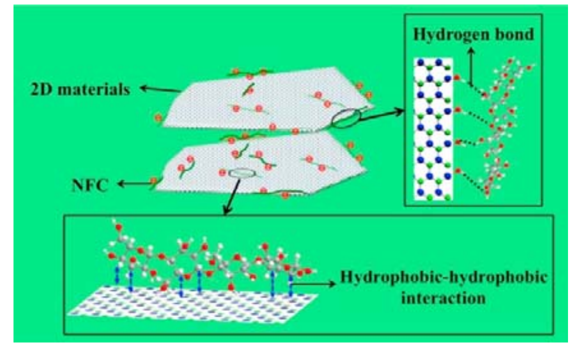
CNF as dispersing agent for carbon nanomaterials



Carbon nanomaterials



Dispersion of carbon materials by CNF

Thermal conductivity of some materials

Materials	Thermal conductivity W/(m·K)	References
Graphite	~3000 (in plane), 6(z-axis)	(Sengupta et al., 2011)
Graphene	2000-5000	(Balandin et al., 2008)
Graphene oxide (GO)	2-1000	(Yang et al., 2019)
Reduced graphene oxide (rGO)	0.14-2.87	(Park et al., 2014; Yang et al., 2019)
Carbon nanotubes	2000~6000	(Han and Fina, 2011)
Silver	429	(Pashayi et al., 2012)
Copper	384	(Tekce et al., 2007)

2.1 Preparation of samples

❑ Preparation of CNF

❖ Preparation of pulp slurry

- Material: HW-BEKP dried pulp
- Preparation of 4 kg of 2 wt% of pulp slurry
- Disintegration: 30,000 revolutions

❖ Grinding

- Grinder: Super Masscolloider, Masuko Sangyo Co., Ltd., Japan
- Gap: −80 μm
- Pass number: 30 passes

Image of the prepared CNF

❑ Preparation of CNF/GNP composites

CNF suspension

Graphene nanoplate (GNP)

homogenization

CNF/GNP mixture

Centrifugation (9000 rpm, 30 min, 3 times)

Details :

- CNF suspension: 0.5 wt%, 100 g
- CNF: GNP ratios: 0.8: 0.5/1.5/2.5
- Homogenization: 1 h, 6000 rpm

❑ Synthesis of CNF/AgNPs composites

CNF suspension

$AgNO_3$ solution

20 min mixing

CNF/$AgNO_3$ mixture

$NaBH_4$ solution

20 min ice incubation

20 min ice incubation

Dropwise addition

20 min reaction after addition

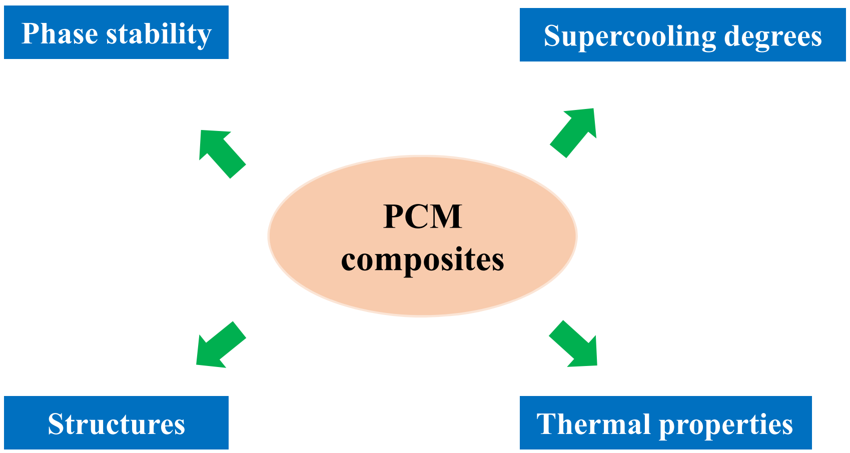
CNF/AgNPs Composites

Centrifugation (9000 rpm, 30 min, 3 times)

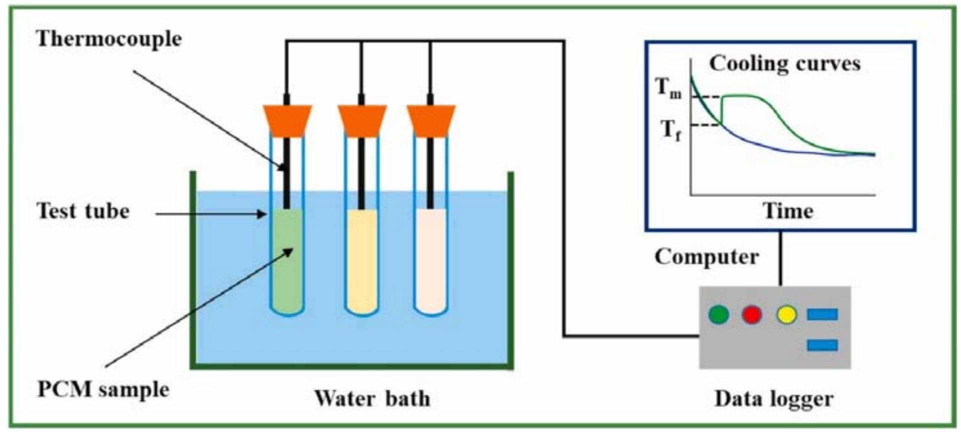
Details :

- CNF suspension: 0.5 wt%, 100 g
- $AgNO_3$ solution: 0.01/0.02/0.03 M, 100 mL
- $NaBH_4$ solution: 0.1 M, 200 mL

2.2 Characterizations



- **Experimental setup of the cooling test**



- **Rheology study**

Bohlin CVO Rheometer
(CVO-100-901, Malvern Instruments Ltd, UK)

- **Calculation of supercooling degree**

$$\Delta T_s = T_m - T_f$$

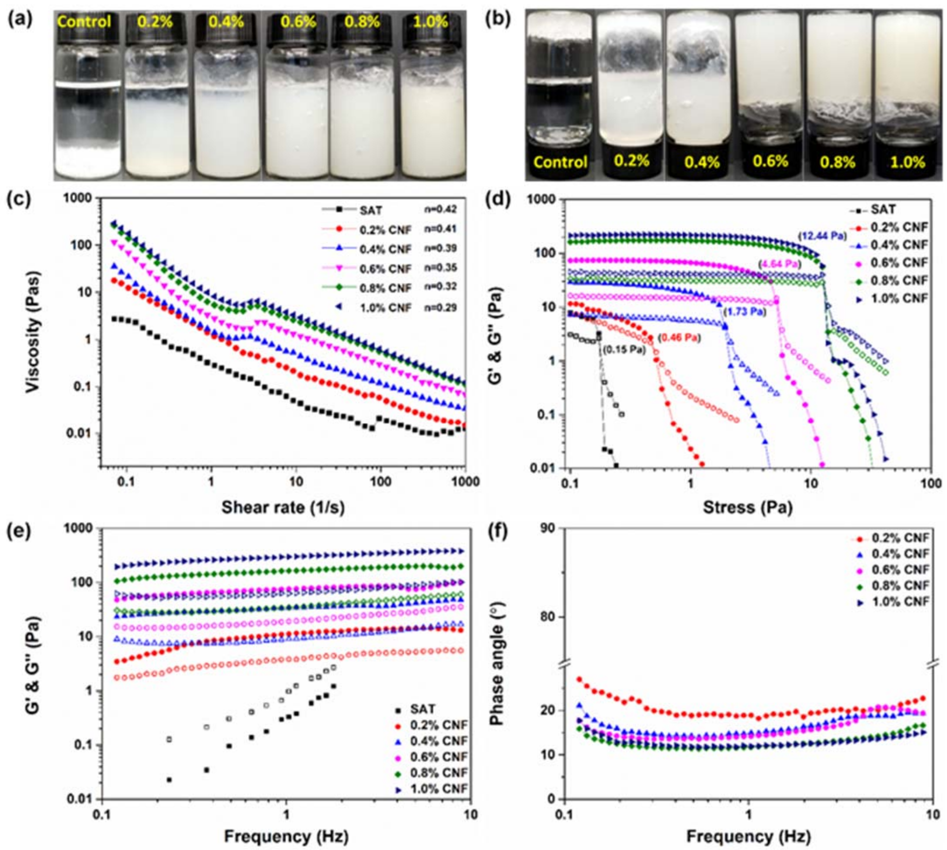
where ΔT_s represents the supercooling degree (°C),

T_m denotes the melting point (°C),

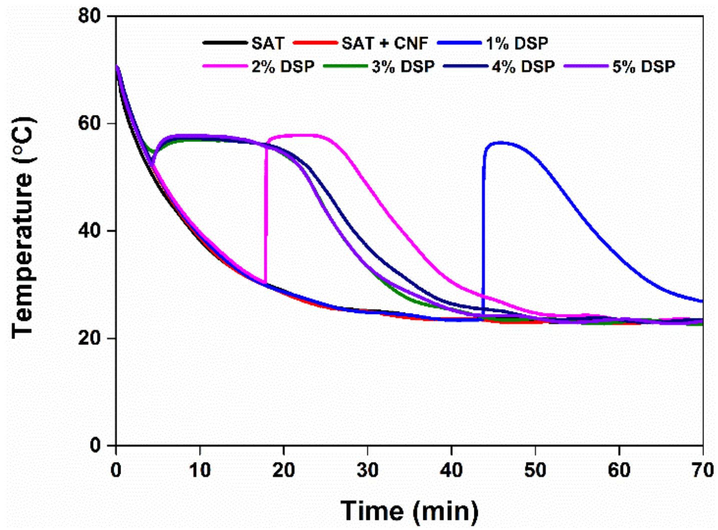
T_f denotes the freezing point (°C).

3. Preparation and application of CNF/GNP composites

❑ Phase stability and its mechanism



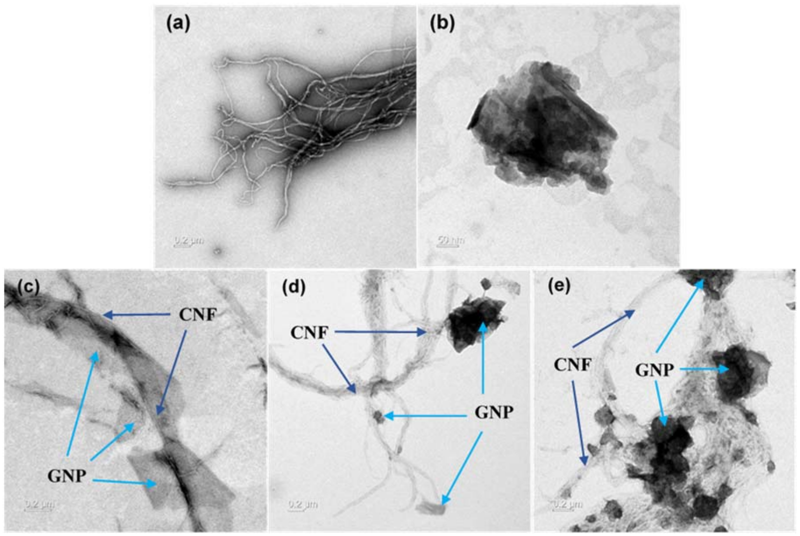
❑ Screening of nucleating agent



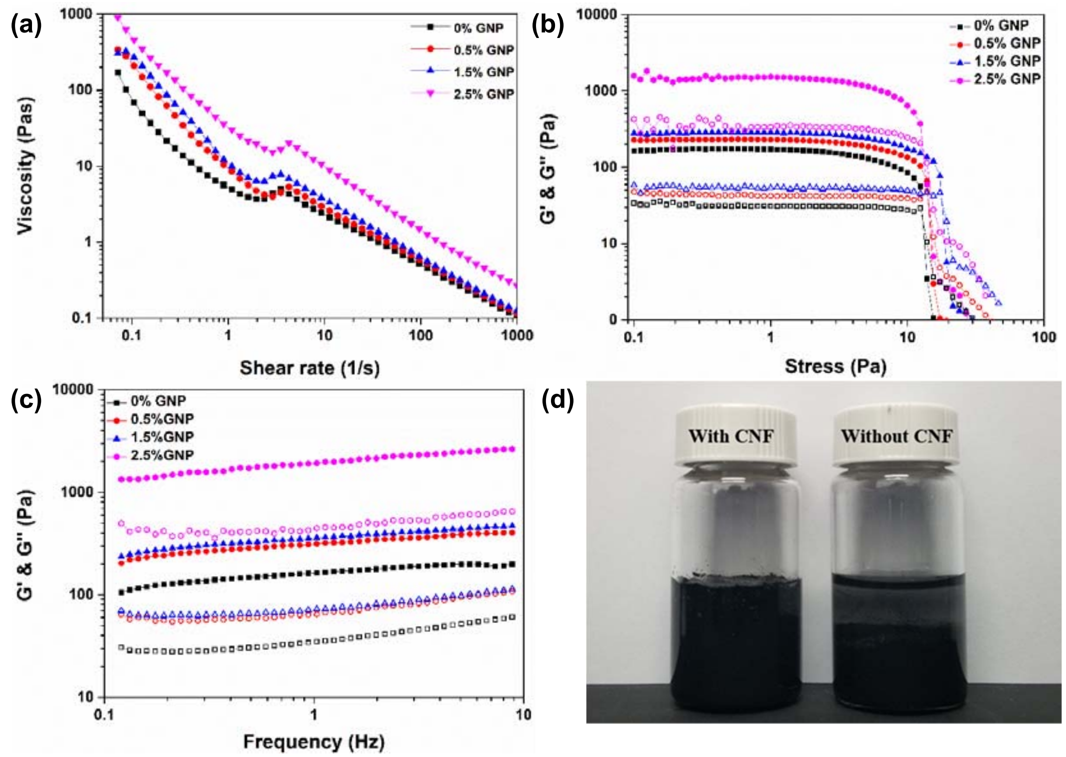
The effect of DSP ($Na_2HPO_4 \cdot 12H_2O$)

❑ Effect of CNF/GNP composites

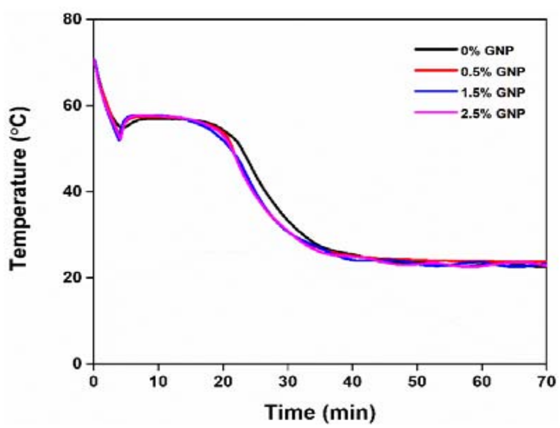
❑ Morphologies of CNF/GNP composites



❑ Effect on rheology and phase stability



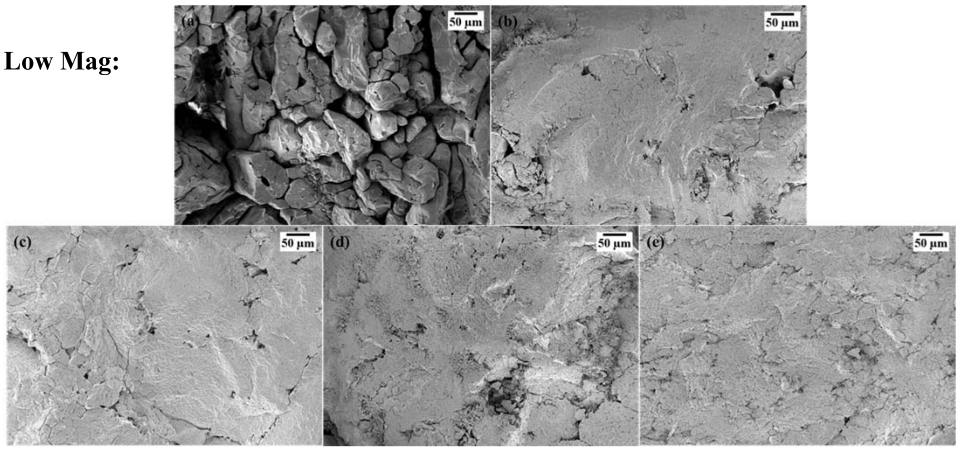
❑ Effect on supercooling



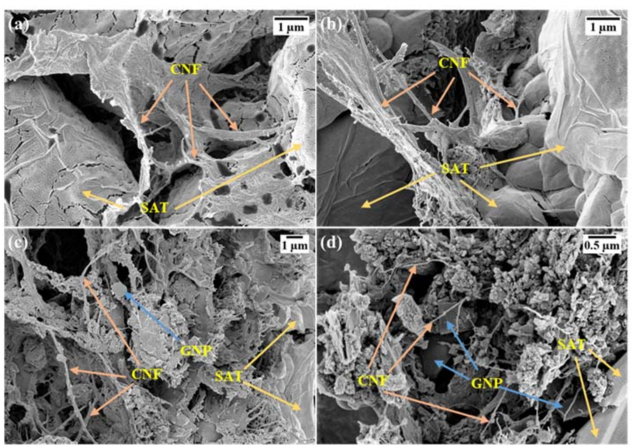
❑ Properties of PCM composites

❑ Structures

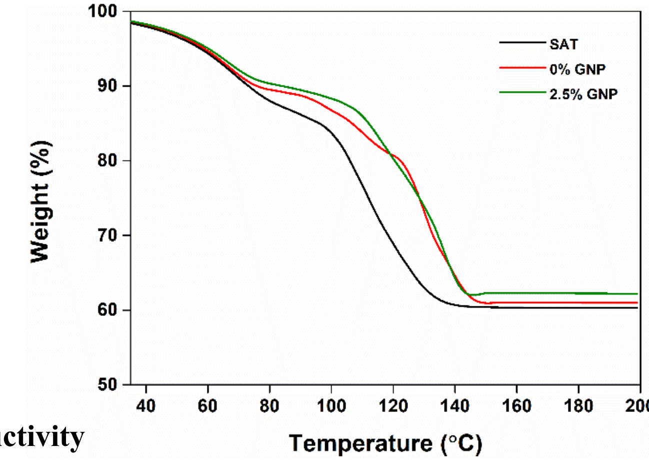
- **Low Mag:**



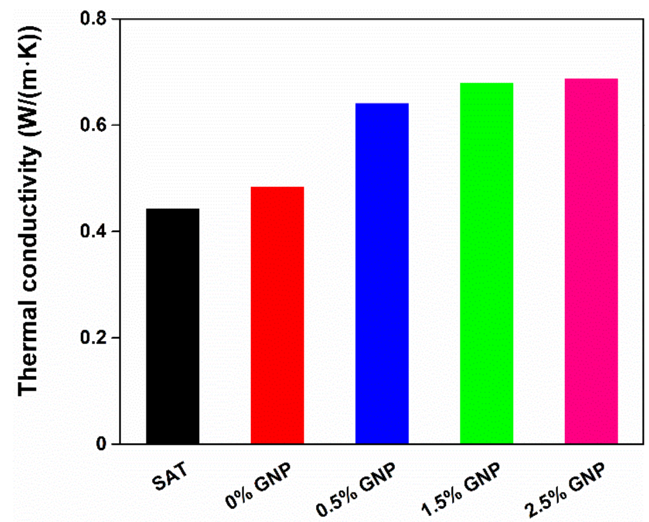
- **High Mag:**



❑ Thermal stability

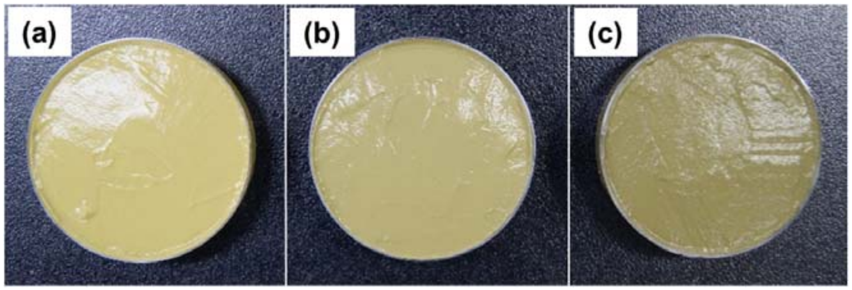


❑ Thermal conductivity



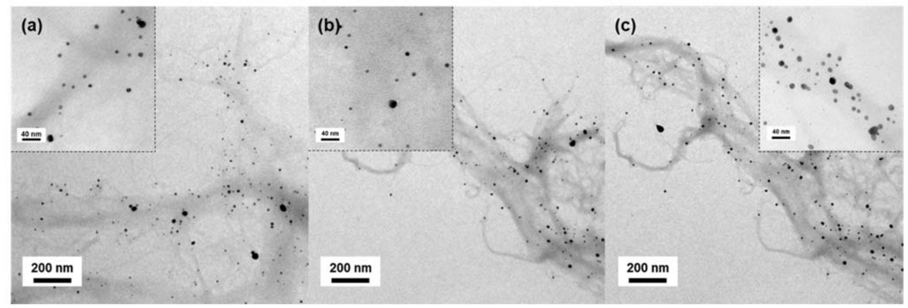
❑ Properties of CNF/AgNPs composites

- **Appearance**



(a) CNF/AgNPs $_{0.01}$, (b) CNF/AgNPs $_{0.02}$ and (c) CNF/AgNPs $_{0.03}$.

- **Morphologies**

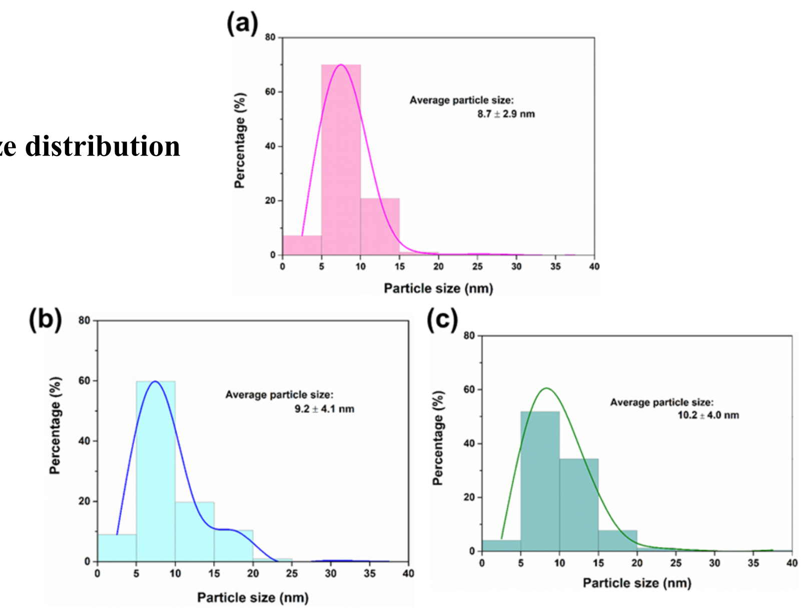


- **Silver content**

Table 1
The silver content of the synthesized CNF/AgNPs composites

Composite	Ag concentration (mg/kg)	Ag content (%)
CNF/AgNPs $_{0.01}$	77.0	7.70
CNF/AgNPs $_{0.02}$	175	17.5
CNF/AgNPs $_{0.03}$	296	29.6

- **Particle size distribution**



❑ Effect of CNF/AgNPs composites

- **Cooling test- the T-history method**

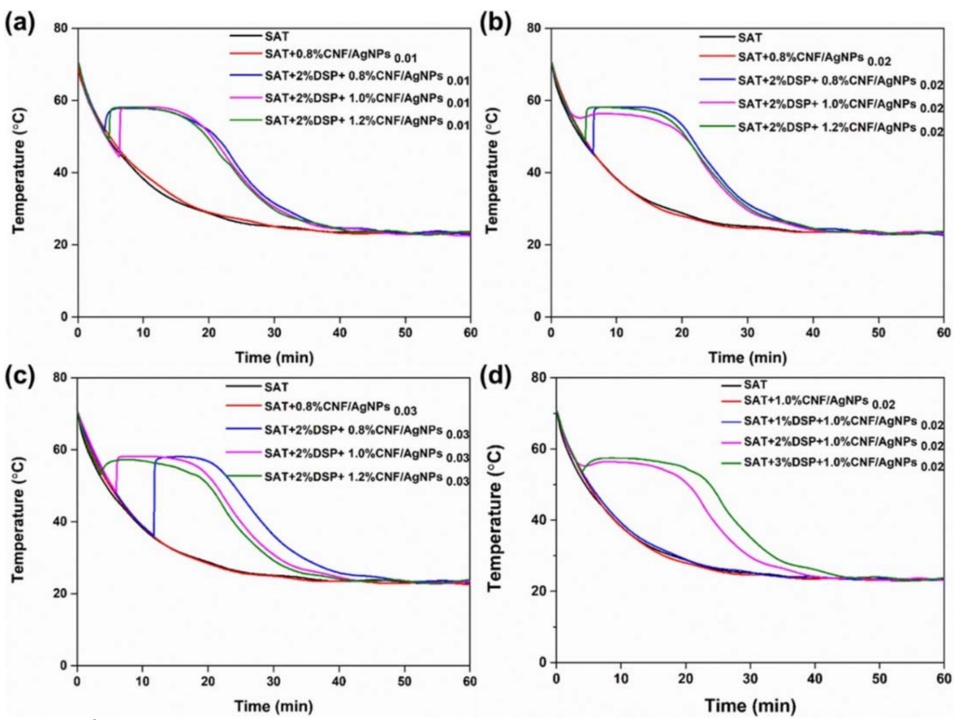
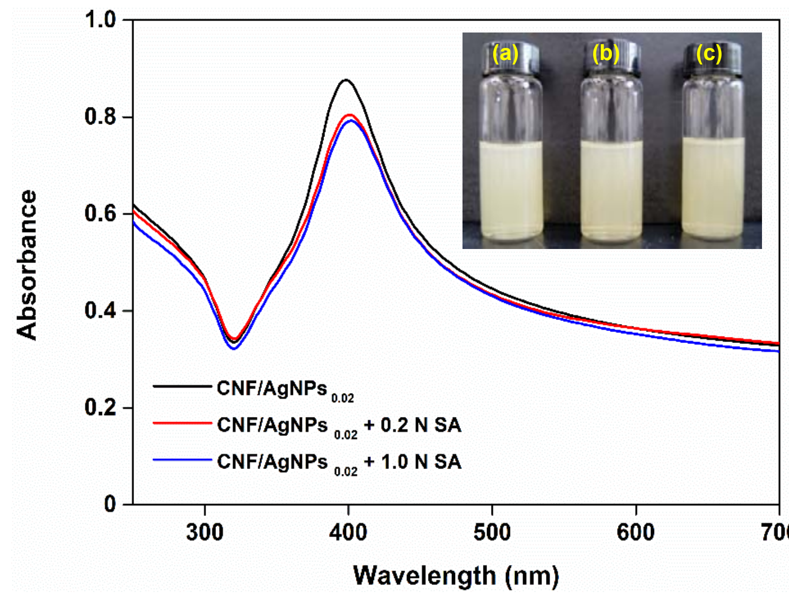


Table 2
Effect of CNF/AgNPs composites: 2% DSP

Dosage (%) / Composites	0.8	1.0	1.2
CNF/AgNPs $_{0.01}$	6.4	13.7	9.2
CNF/AgNPs $_{0.02}$	12.9	**1.2**	9.2
CNF/AgNPs $_{0.03}$	21.9	7.8	3.9

- **Stability of CNF/AgNPs composites**



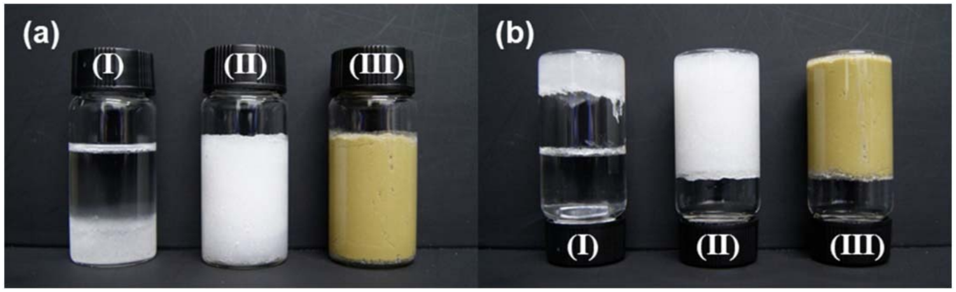
- **Supercooling degrees**

Table 3
Effect of the dosage of DSP: 1% CNF/AgNPs $_{0.02}$

Dosage of DSP (%)	0	1	2	3
Supercooling degree (ºC)	35	35	**1.2**	3.8

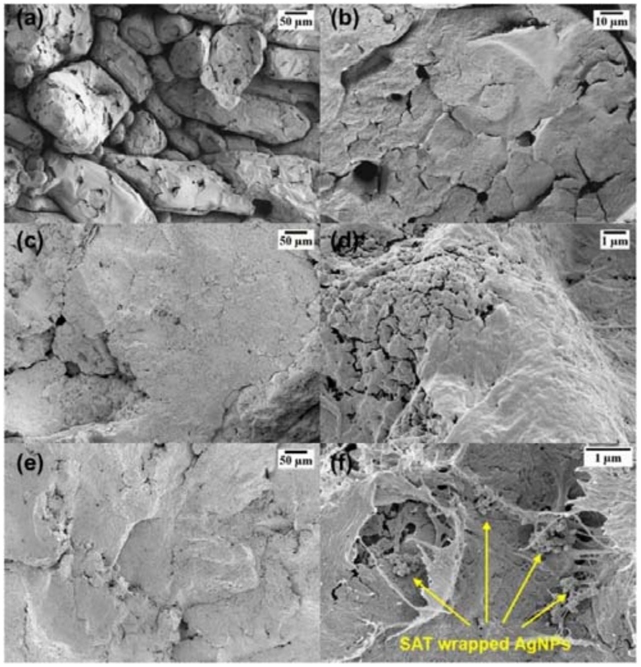
❑ Properties of PCM composites

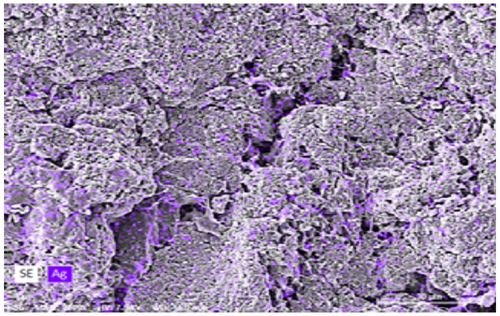
- **Phase stability**



(I) SAT, (II) PCM@CNF and (III) PCM@CNF/AgNPs $_{0.02}$.

- **Structures**

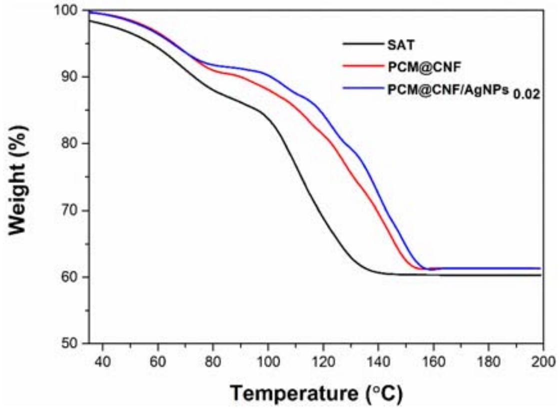




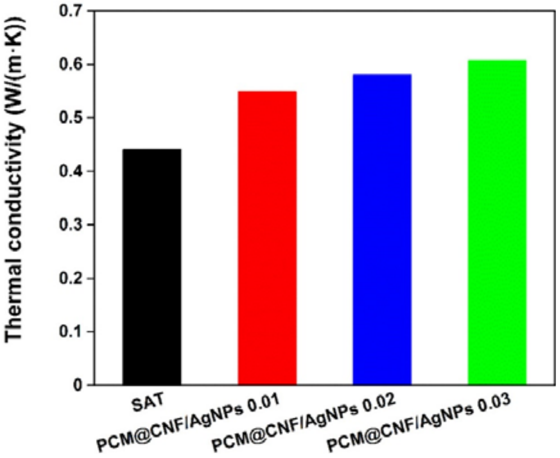
Distribution of AgNPs in PCM

*(a) and (b) SAT
(c) and (d) PCM@CNF
(e) and (f) PCM@CNF/AgNPs $_{0.02}$.

- **Thermal stability**



- **Thermal conductivity**



5. Conclusions

- The drawbacks of SAT as a PCM for thermal energy storage were successfully addressed by the use of CNF-based composites.

1. CNF acted as the thickening agent of SAT and the dispersing agent of GNP and silver nanoparticles.

2. The use of CNF-based composites provided phase stability to SAT, eliminating the phase separation problem.

3. 2% DSP and 1% CNF/AgNPs $_{0.02}$ synergistically decreased the supercooling degree of SAT to 1.2 °C.

4. The thermal stability and thermal conductivity of the prepared PCM composites improved.

Thank you for your attention !

<u>TAPPI Nano 2021 Virtual Conference</u>

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Shen, Z., Kwon, S., Lee, H. L., Toivakka, M., & Oh, K. (2021). *Sol. Energy Mater. Sol. Cells*, *225*, 111028.

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❑ Sources of images

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