



# Superwetting polypropylene aerogel supported form-stable phase change materials with extremely high organics loading and enhanced thermal conductivity



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## ABSTRACT

The development of high efficient materials or devices for storage and utilization of sustainable thermal energy should be of great importance in alleviating energy crisis. Herein, we reported the fabrication of superwetting polypropylene (PP) aerogel as the support materials for construction of form-stable phase change materials (PCMs) composites. Due to its abundant porosity, light weight of aerogel in nature, inherent superhydrophobic and superoleophilic properties, lipophilic organic PCMs can be loaded into PP aerogel (PP/PCM) with a high PCMs loading of up to 1060 wt%, which is nearly two orders of magnitudes higher than those mostly reported form-stable PCMs systems. The PP/PCM composites show high latent heat in the range of 141.1 kJ kg<sup>-1</sup> to 159.5 kJ kg<sup>-1</sup> and excellent thermal stability and recyclability where their latent heat nearly remains unchanged even after 50 times of melting/freezing cycles. Results obtained from the X-ray diffraction (XRD) show that the incorporation of organic PCMs into PP aerogel network decreases the crystal size of PCMs in the composites. More interestingly, the PP/PCM composites show an enhanced thermal conductivity, in the case of PP/Paraffin composite, which is over two times of that of paraffin. Having the advantages of low cost and abundant resource of PP, simple preparatory process, high PCMs loading, good stability, recyclability and thermal conductivity, this the PP/PCM composites may have great potential for renewable energy saving applications.

## 1. Introduction

Every year, huge amounts of energy were consumed all over around the world. In response to the energy crisis of fossil fuels as well as emerging ecological concerns and global warming, the exploitation of clean, renewable, and sustainable energy resource and techniques has become increasingly important than ever. So far, a number of new energy resources have been exploited, for example, solar energy, wind energy and nuclear energy, etc. However, there are still a lot of issues, including energy intermittence, geographical restrictions, etc., for utilization of those mentioned energy remain to be solved. Therefore, the development of high efficient materials or devices for capture and storage of that energy should be of great significance.

Phase change materials (PCMs) are a kind of materials with a high heat of fusion which, melting and solidifying at a certain temperature, are capable of storing and releasing large amounts of thermal energy when their phase changes from solid state to liquid state or vice versa.

Also, this enables thermal energy being stored from one process or period of time and used at a later point in time or transferred to a different location, which shows great potential for various applications such as solar energy saving [1–3], industrial waste heat recovery [4,5], building energy saving [6,7], electronic temperature control equipment [8] and functionally thermal fluid [9], etc.

To date, a number of materials such as inorganic compounds, organic compounds, and their mixtures can be used as PCMs, including hydrated salts [10], paraffin [11,12], fatty acids [13], and polyethylene glycol (PEG) [14,15]. Compared with inorganic PCMs, organic PCMs have the characteristic of low corrosion and melting/freezing cycles without phase segregation, which have been widely used in thermal energy saving systems. In the most cases, however, the direct use of these organic PCMs has the limitations for the leakage of the liquid phase above their melting point. To address this issue, micro-encapsulated phase change materials with organic PCMs as core and microcapsules as shell have been proven to be an efficient strategy and

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thus have been well investigated. However, the drawbacks for the microcapsule method relied in the need of multistep procedures, complicated techniques and relative high cost, thus hindering their practical applications. In contrast, direct storing the PCMs into porous support materials to form form-stable PCM composites should be one of promising remedies to this issue. To date, several kinds of porous materials including gypsum [6,16], diatomite [17], graphene aerogel [18–20], SiO<sub>2</sub> [21,22], conjugated microporous polymers [23] and ceramic composites [24] have been used to fabricate form-stable PCM composites by means of natural immersion approach. Along this line, we have recently developed the development of several kinds of porous materials with superhydrophobic and superoleophilic wettability, including superwetting graphene-nickel foam (G-NF) [25], conjugated microporous polymers (CMPs) [23] and spongy attapulgite (s-ATP) [26], for construction of form-stable PCM composites with enhanced significantly enhanced affinity of lipophilic organic PCMs (e.g. Paraffin) to support materials

In a continuation of our previous works on PCMs [23,26,27], herein, we report the first example of polypropylene (PP) based aerogel with superwetting property as porous medium for fabrication of form-stable PCM composites (PP/PCM). Our primary design for construction of such superwetting PP aerogel was based on the following three main aspects: (1) The superhydrophobic and superoleophilic properties of the PP based aerogel originated from its inherent lipophilic chemistry in combination with porous morphology, which is easy to be fabricated and thus quite different from those artificial superwetting support materials that usually need complicated and multistep to prepare. (2) Compared with those reported porous materials for preparation of form-stable PCM composites which are usually capable of loading the PCMs in the range from ten percent to tens of percent [28,29], and the results of PP/PCM composites are at least one order of magnitude higher owing to its light weight in nature of aerogel. (3) The thermal conductivity of the PP/PCM composites was notably elevated over one fold after the addition of PP as compared with that of the pure PCMs. We suggest that such superwetting PP aerogel may find diverse applications for thermal energy saving systems. On the other hand, the findings of this study may also provide useful guidance for future design and creation of high performance form-stable PCMs composites.

## 2. Experimental

### 2.1. Materials

Isotactic polypropylene (PP,  $M_w = \sim 250,000$ ) was obtained from Sigma-Aldrich Co. LLC. P-xylene was purchased from Shanghai Zhongqin Chemical Reagent Co., Ltd. Isopropyl alcohol was supplied by Tianjin Fuyu Fine Chemical Co., Ltd. Paraffin was used as phase change energy storage material and ordered from Shanghai Huashen Rehabilitation Equipment Co., Ltd. Myristic acid (MA) and stearic acid (SA) were purchased from BASF chemical Co. Let. All chemicals were used as received without purification.

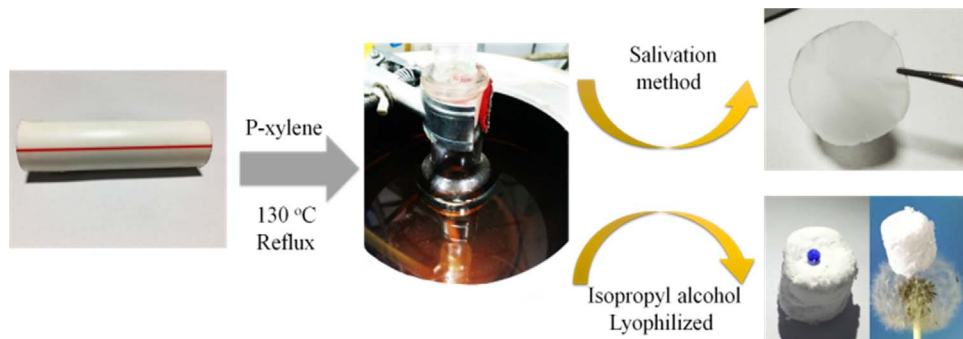


Fig. 1. The preparation of polypropylene aerogel and film.

### 2.2. Preparation of PP aerogel and film support materials

Isotactic polypropylene solution (20 mg mL<sup>-1</sup>) was prepared by adding granular PP and 10 mL of p-xylene in a round-bottomed flask under silicone oil bath at 130 °C [30]. When granular PP was fully dissolved, a homogeneous solution was formed. Then, different operation methods were adopted to fabricate the aerogel and film. As for aerogel, the isopropyl alcohol was added into the solution, and then the mixtures were precipitated and lyophilized as aerogel for latter process. The film was obtained through salivation method.

### 2.3. Preparation of phase change materials composites

A certain amount of PP aerogel was immersed into a small beaker filled with paraffin in water bath or dry oven at 90 °C. The aerogel was permeated for just a short moment. Afterwards, the treated PP/Paraffin composites were taken out and dried in the oven at 90 °C to remove the excessive paraffin until the weight loss keeping constant. The procedures are same for preparation of PP/MA and PP/SA. The following equation was used to calculate the loading rate for PP/PCM composites:

$$\phi = \frac{m_1 - m_0}{m_0}$$

where  $m_0$  is the weight before loading of PCMs,  $m_1$  is the weight after loading of PCMs and  $\Phi$  is the loading rate, respectively.

### 2.4. Characterization

Surface morphology was observed on a JSM-6701F cold field emission scanning electron microscope (SEM). All samples were gold coated before analysis. Energy Dispersive Spectrometer (EDS) analysis was performed on a cold field emission scanning electron microscope (Oxford X-Max). The X-ray diffraction (XRD) was performed on a Rigaku D/Max-2400 diffractometer with a Cu tube source and scans were taken from 2 $\theta$  at 2° to 80°. The Brunauer-Emmett-Teller (BET) surface area and the porous volume of the PP aerogel were detected with a nitrogen adsorption/desorption isotherm measured at 77 K using a physisorption analyzer (ASAP 2020, Micromeritics). The water contact angle (CA) was measured on a contact anglemeter (DSA100, Kruss). Differential scanning calorimeter (DSC, 200F3) was utilized to learn about their thermodynamic properties. The samples were detected from 20 °C to 120 °C with a heating-cooling rate of 5 °C min<sup>-1</sup> in nitrogen atmosphere at a flow rate of 10 mL min<sup>-1</sup>. The thermal conductivity of PP/PCM composites were investigated on flash method thermal analyzer (LFA 447, Netzsch).

## 3. Results and discussion

In this work, isotactic polypropylene or waste polypropylene-based materials, which is commercially available and widely used in industry, was used as raw material for preparation of porous support material to fabricate the PCM composites. To this end, isotactic polypropylene (or

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