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Fabrication of thermal energy storage wood based on graphene aerogel encapsulated polyethylene glycol as phase change material

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Abstract

Thermal energy storage wood (TESW) was fabricated by using graphene aerogel encapsulated polyethylene glycol (PEG) as phase change material and wood as the matrix. The microstructure of TESW was investigated by scanning electron microscope (SEM), the thermal properties of TESW was determined by differential scanning calorimetry (DSC), thermal gravimetric analysis (TG) and laser flash diffusivity apparatus (LFA). The results showed that: (1) graphene aerogel (GA) encapsulated PEG composite was founded in the lumens of wood, there was no apparent interface between PEG and graphene aerogel; (2) the melting and freezing enthalpy of TESW were 11.81 and 27.91 J g⁻¹, respectively. The melting and freezing point were 20 °C and 15 °C, respectively, which were suitable for human comfortable temperature; (3) incorporation of graphene aerogel improved the thermal conductivity of TESW apparently. Thermal conductivity of TESW was 0.374 W (m·K)⁻¹, which increased about 274% compared to pure wood; (4) TG and hygroscopicity test indicated that the TESW had excellent thermal and dimensional stability. The TESW was suggested as energy conservation building material for indoor temperature regulating due to its comfortable phase change temperature and prior latent heat.

Abbreviations

TESW Thermal energy storage wood;
GA Graphene aerogel;
PEG Polyethylene glycol;
PCMs Phase change materials.

1. Introduction

Energy consumption is becoming the crucial factor to restrict economic development since human entered the industrial society. In particular, the increasing building energy consumption brings a lot of environmental problems with the growth of population [1–5]. Therefore, energy saving and conversion become a worldwide topic [6, 7]. Phase change materials (PCMs) are an energy-saving material which can release or absorb thermal energy through phase change within a certain temperature range. PCMs have been applied in building-saving area to create a comfortable indoor environment and realize energy conservation [8–10]. Solid-liquid PCMs, including paraffin wax, polyethylene glycol and fatty acid, have been widely used due to their high heat storage density and stability [11–14]. However, the leakage and low thermal conductivity are still serious problems to restrict their applications [15, 16].

High thermal conductivity phase change material has been paid extensive attention by incorporating excellent heat transfer graphene (3100–5300 W m⁻¹ K⁻¹) [17–20]. Mehrail et al improved the thermal conductivity of paraffin by adding graphite oxide (GO) [21]. Results showed that PCM composite with palmitic
acid and GO exhibited high thermal conductivity about 1.03 W m$^{-1}$ K$^{-1}$. Wang et al fabricated solid-solid phase change material by grafting PGE on the surface of GO. They indicated GO improved the thermal conductivity of the composite obviously [22]. Graphene aerogel (GA) with uniform distribution and excellent network structure also attracted high attention compared to GO. Yang et al impregnated the hybrid graphene aerogels with polyethylene glycol in order to improve the thermal conductivity of PCMs. They reported the thermal conductivity of PCMs reached 1.43 W m$^{-1}$ K$^{-1}$ when adding 1.8 wt% graphene nanoplate [23].

Porous material is one of the suitable materials to solve the leakage problem of PCMs [24–26]. Sedat et al produced thermal energy storage composite by incorporating PEG into diatomite [27]. The results showed that diatomite still reserved 50% PEG after suffered the phase change process. Qian et al infiltrated PEG into hexagonal boron nitride porous scaffolds to improve the thermal conductivity and overcome the problem of leakage [28]. Wood is a natural anisotropy porous material which can also be used for encapsulating PCMs [29–31]. Yang et al prepared a reversible thermochromic composite with delignified wood [32]. They reported that the composite showed prior phase change property which had suitable phase change temperature, large latent heat, good thermal reliability and stability. However, the thermal conductivity of composite is only 0.216 W (m K)$^{-1}$ at 25 °C owing to the thermal insulation of wood. Li et al prepared a composite by impregnating wood with polyethylene glycol for energy storage and conversion [33]. They reported that the WPG increased by 36.18% when wood treated with 60 wt% PEG for 8 d. However, after 400 thermal cycles, the melting and freezing temperatures of composite varied about 2.54 °C and 1.39 °C due to the leakage of PEG. Barreneche et al filled paraffin wax into wood to prepare a novel PCM/wood composite, but results showed that leakage still appeared due to the limited leak tightness of wood [34]. These researches indicated that encapsulation by using porous materials is a convenient and efficient method for solving the leakage of PCMs. But the leakage still appeared during the phase change process and low thermal conductivity restrict their application, in particular, when use wood as the encapsulating matrix.

Thus, we aimed to prepare a thermal energy storage wood by using graphene aerogel encapsulated polyethylene glycol as phase change material and wood as the matrix to prevent leakage. The process to fabricate TESW was illustrated in scheme 1. In the study, graphene aerogel in the composite was prepared by hydrothermal method via using graphene oxide as raw materials and Vitamin C (Vc) as the reducing agent. PEG-800 was acted as phase change material and was encapsulated by graphene aerogel. The prepared composite was investigated by scanning electron microscope (SEM) to explore the morphology of TESW. The thermal performance was analyzed by differential scanning calorimetry (DSC), thermal gravimetric analysis (TG) and laser flash diffusivity apparatus (LFA). Physical properties were also determined for practical building applications.
2. Experimental section

2.1. Materials
Polyethylene glycol-800 was supported by Aladdin industrial corporation (China), graphene oxide was provided by Shenzhen Turing evolution technology corporation Co., Ltd, Vitamin c (Vc) was purchased from Shiyao Group Weisheng Pharmaceutical Industry (Shijiazhuang) Co., Ltd Poplar wood (Populus alba Linn.) was provided by Shengmeida wooden corporation.

2.2. Preparation of thermal energy storage wood
The wood specimens (20 × 20 × 20 mm) were divided into 9 groups and 14 samples in each group. First, PEG-800 was dissolved in distilled water and followed by graphene oxide and 0.5 wt% Vc. The mixture was treated by ultrasonic for 30 min at 30 °C. Then, all samples were soaked in the mixture to carry out the vacuum impregnation at 0.25 Mpa for 30 min. After heating for 180 min, the samples were cleaned and dried at 60 °C for 48 h. In order to compare with the TESW, the control group was prepared by impregnating PEG-800 into pure wood (PD). The Specific experimental arrangements were shown in table 1.

2.3. Characterization
The morphology of pure wood and TESW were investigated by SEM (6380LV, Japan Electronics Corporation, Japan) and all samples were sprayed with gold powder before observation. The weight change of TESW was calculated according to the following formula (W is the weight of TESW, Wt is the weight of pure wood).

\[
\text{Weight percentage gain (WPG)} = \left(\frac{W - W_t}{W_t}\right) \times 100\%
\]

The shrinkage of TESW was determined according to the standard ISO 13061-13:2016 [35] and the swell rate of TESW was tested according to the standard ISO 13061-15:2017 [36].

Thermal property including enthalpy and phase change temperature was evaluated by DSC (204 Phoenix, Netzsch, Germany). The heating or cooling temperature rate was controlled at 5 °C min⁻¹ under nitrogen atmosphere and the temperature range was −10 to 60 °C. Thermal stability of TESW were measured by TG (DTG-60H, Shimadzu, Japan) in the temperature range of 20 °C - 600 °C at the rate of 10 °C min⁻¹ under nitrogen atmosphere.

Thermal conductivity of the composites were evaluated the by LFA (LFA467, Netzsch, Germany at 25 °C. The density of samples (10 × 10 × 1 mm) was determined by Mettler Toledo model DE50 vibrating tube densimeter. Each sample was measured 5 times.

3. Results and discussion

3.1. Microstructure of TESW
Figure 1 shows the microstructure of pure wood and TESW. As shown in figures 1(a) and (b), poplar wood is a natural porous material with a large number of pores which range from 10 to 400 μm. These pores, including
vessel, fiber and pit, provide potential for encapsulating PCM. The impregnation mixture of phase change material consisted of PEG-800 and graphene oxide, in which the average particle size of PEG-800 is approximately 1.2 nm and the size of graphene oxide is below 1 μm. Therefore, it is possible for impregnating the mixture of PEG and graphene oxide into wood. After impregnation, PEG/GA entered into the vessels successfully and even some pits were also been filled (figures 1(c) and (d)). The incorporated PEG was encapsulated by GA with its net structure and there was no apparent interface between GA and PEG, which meant a good compatibility. Furthermore, the leakage problem of melting PEG was solved effectively due to the cross-linking structure of GA and the capillary effect of wood.

3.2. Weight gain rate of TESW

Weight percentage gain (WPG) is a visual indicator to reflect the latent heat of TESW because wood itself has no phase change ability and enthalpy of TESW is mainly derived from the filler. The relationship between WPG, PEG, GO and temperature was explored by establishing mathematical model. The weight gain rate of samples were measured and recorded under different processing conditions. According to the scatter diagrams of samples, the fitting equation was fitted and optimized by using Matlab, the image of mathematical model was depicted then.

\[
WPG(\%) = \alpha \times x_1^{\beta} \times x_2^{\gamma} \times x_3^{\nu}, \quad \alpha = 2.3585, \quad \beta = 0.5898, \quad \gamma = 0.1174, \quad \nu = 0.2057
\]

Where \(x_1\) is the concentration of PEG, \(x_2\) is the concentration of GO and \(x_3\) is the bath-water temperature.
As seen in figure 2, it is apparent that the concentration of GO and temperature almost had no effect on WPG. Because the mass fraction of graphene oxide was very low and the temperature we chose did not influence the formation of GA effectively. But the WPG increased sharply with increasing PEG concentration. WPG of P_{60}G_{0.4}T_{80} reached to 58.25% when the concentration of PEG was 60%, which also indicated that PEG and GO has impregnated into the wood effectively.

3.3. Dimensional stability of TESW

Influence of different components on the TESW linear shrinkage is shown in figure 3 and table 2. The minimum linear shrinkage was 0.56% when the temperature at 80 °C, the mass fraction of PEG at 60% and GO at 0.3%. PEG was the strongest impact on the linear shrinkage extent of TESW compared to the other two factors. The reason could be attributed to the excellent bulking function of PEG which filled the microstructure of wood and prevented the moving of water [37, 38]. The influence of GO was limited due to its low addition amount though it formed a cross-linking structure which could support the wood avoiding deformation. And for temperature, it also influenced the linear shrinkage slightly because it mainly related to the formation of GA [39].

3.4. Thermal energy storage property

Figure 4 shows the DSC curves of PEG-800, P_{60}G_{0.4}T_{80} and pure wood. There was no endothermic or exothermic peak of wood during temperature changing process, which also indicated that pure wood had no contribution to the enthalpy of TESW. The melting and freezing enthalpy of P_{60}G_{0.4}T_{80} were 11.81 J g$^{-1}$ and 27.91 J g$^{-1}$, respectively, which were much lower compared to PEG-800. The reason could be attributed to the
formation of rotator and the broken crystalline structure of PEG after impregnation. Also, PEG was the only phase change material in wood and its low mass fraction led to the lower enthalpy of TESW. The melting and freezing point of P60G0.4T80 were 20 and 15 °C, respectively, which were a little different from pure PEG. PEG was divided into small droplet and the crystalline structure was also broken after incorporated into wood. So during freezing process, the decreasing PEG crystal nucleus due to volume change of PEG droplet, led to a supercooling phenomenon. And during melting process, less thermal energy was needed because of the formation of rotator and the broken crystalline structure of PEG, so the melting point of TESW was lower. The phase change temperature range of TESW was about 15 °C to 20 °C, which was comfortable for human indoor temperature.

3.5. Thermal stability of TESW

The TG curves of PEG-800, GO, PD, pure wood and TESWs are shown in figure 5. There was only one weight loss stage for PEG-800 in the range from 300 °C to 400 °C. And pure wood had two decomposed stages, one was the evaporation of moisture at 30 °C and another was mainly the decomposition of cellulose, hemi-cellulose and lignin. After impregnation, TESWs showed two-step degradation, the first slight weight loss from 30 °C to 60 °C due to the evaporation of residual moisture. And the sharp weight loss from 230 °C to 400 °C was attributed to the breakage of wood composition and the degradation of PEG. The weight loss of P60G0.4T80 just about 3% at 230 °C, which indicated TESWs have excellent thermal stability when using under indoor temperature.
3.6. Thermal conductivity of TESW

Thermal conductivity of pure wood, PEG-800, PD and P60G0.4T80 are shown in figure 6. Thermal conductivity of PD was 0.186 W (m·K)−1, which increased by 86% compared to pure wood. The reason was that PEG served as a higher thermal conductivity material filled the wood pores and formed a continuous heat transfer network. After the addition of GO, the thermal conductivity of P60G0.4T80 reached to 0.374 W (m·K)−1, which increased about 274% than pure wood. One reason was the high thermal conductivity of GO and another was benefited from the special three-dimensional network structure of GA [45]. TESWs with high thermal conductivity are beneficial for rapid thermal energy exchange to realize the regulation of indoor temperature.

3.7. Shape-stability and thermal cycling stability

The application of composite phase change materials is hindered by the liquid leakage during phase transition. Thus, shape-stability and thermal cycling stability are vital factors to evaluate the practicability of composite phase change materials. The image of TESW after leakage test is shown in figure 7. PEG was completely melted after 60 °C heat treatment for 30 min and a slight leakage was observed for GA encapsulated PEG. But TESW had no liquid leakage during the heat treatment which is benefited by the form support of wood and GA with anisotropic porous structure. Thermal cycling stability of TESW was also explored by using DSC after 100 cycles (figure 8). The melting and freezing enthalpy of P60G0.4T80-100 were respectively 19.8 J g−1 and 17.8 J g−1 which
were just slightly lower than $P_{60,G_0.1T_{80}}$. So it further indicated that TESW has great shape stability and outstanding thermal cycling stability for building application.

4. Conclusion

Thermal energy storage wood (TESW) was fabricated by using graphene aerogel encapsulated polyethylene glycol (PEG) as phase change material and wood as the matrix. Graphene aerogel and PEG entered into the lumens of wood successfully, there was no apparent interface between PEG and graphene aerogel. Addition of PEG and GA improved the dimensional stability of TESW apparently due to their filling effect. TESW showed acceptable latent heat and suitable phase change temperature which fits the human comfortable temperature range. LFA test showed TESW had outstanding thermal conductivity, which increased 274% compared to pure wood. TG test indicated the TESW had excellent thermal stability when used under indoor environment. The prepared TESW was suggested as energy conservation building material for indoor temperature regulating due to its the comfortable phase change temperature and prior thermal enthalpy.
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Author contributions

Xianxian Lin: designed and carried out experiments, Writing - Original Draft.
Shifang Jia: carried out experiments.
Huimin Cao: analyzed experimental results.
Wenbin Wang: analyzed experimental results.
Xi Guo: provided experimental instruments and valuable suggestions.
Weisheng Sun: provided experimental instruments and valuable suggestions.

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