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1 **Preparation and characterization of expanded perlite/paraffin composite with enhanced**

2 **thermal conductivity and leakage-bearing properties by graphene oxide**

3

4 *Zeyu LU[1] , Dongshuai HOU[2, *], Biwan XU[1], Zongjin LI[1]*

5 *1. Department of Civil and Environmental Engineering, The Hong Kong University of Science and*

6 *Technology, Hong Kong, China.*

7 *2. Department of Civil Engineering, Qingdao Technological University (Cooperative Innovation Center*

8 *of Engineering Construction and Safety in Shandong Blue Economic Zone), Qingdao, China*

9 *Tel.: +852-9162-6614; Fax: +852-2358-1534.*

10 ** Corresponding author: Dongshuai HOU; E-mail: dhou@ust.hk;*

11

12   **Abstract**

13 A novel phase change materials (PCMs) of expanded perlite/paraffin/graphene oxide

14 (EP/PA/GO) with enhanced thermal conductivity and leakage-bearing properties was fabricated

15 by depositing GO films on the surface of the EP/PA composite. The as-prepared EP/PA/GO

16 composite was characterized by using Differential scanning calorimetry (DSC),

17 Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and

18 Scanning electron microscopy (SEM) techniques. The experimental results indicated that due to

19 the small loading of the GO incorporation within 0.5 wt.%, the EP/PA/GO composite showed a

20 small latent heat capacity and weight loss, and the thermal conductivity significantly increased

21 with increasing content of GO up to 0.5 wt. %. The heat storage/release performance test results

22 demonstrated that the EP/PA composite with 0.5 wt. % GO had 2 times faster heat

23 storage/release rate compared to the EP/PA composite because of the enhanced thermal

24 conductivity. In addition, the FTIR and TGA results indicated that the EP/PA/GO composite had

25 a good chemical compatibility and thermal stability. More importantly, the GO films covering the

26 surface of the EP/PA composite can greatly prevent the leakage problems of the molten paraffin.

27 No leakage of paraffin occurred even after thermal cycling 3000 times. Therefore, the EP/PA/GO

28 composite has a great potential for thermal energy storage applications due to its enhanced

29 thermal properties, good leakage-bearing properties and excellent chemical compatibility.

30

31   *Keywords*: phase change materials; graphene oxide; thermal conductivity; leakage-bearing

32   properties.

33

34   **1. Introduction**

35   Latent thermal energy storage (LTES) is a promising approach to improve solar energy

36   utilization and minimize energy dissipation in buildings due to its high energy storage density

37   and capacity at constant temperature [1, 2]. Phase change materials (PCMs) are widely used in

38   the LTES system and have been receiving great attention for various applications in solar heating

39   systems, building energy conservation and air-conditioning systems [1, 3-5]. PCMs mainly

40   include inorganic PCMs such as alloys, melted salts and crystalline hydrated salts, and organic

41   PCMs such as paraffin, fatty acids/esters and lauric acid [6, 7]. However, the leakage problem

42   after melting and the lower thermal conductivity of PCMs are the two main drawbacks limiting

43   wide application. One way to prevent the leakage problem is by using micro- and macro-

44   encapsulation methods, including interfacial polymerisation, emulsion polymerization and situ

45   polymerization [8, 9]. PCMs form the core with a polymer shell to maintain the shape and

46   protect the PCMs from leakage. However, the aging, cost and lower thermal conductivity of

47   encapsulation shells have been the biggest concern for this method. The other way is to

48   impregnate PCMs into porous materials, such as diatomite [10, 11] and expanded perlite [7, 12].

49   Lu et al.[13, 14] have fabricated a form-stable expanded perlite/paraffin (EP/PA) composite by

50   absorbing paraffin into porous networks of expanded perlite, resulting in good thermal energy

51   storage, thermal stability and thermal reliability. The leakage problem can be resolved to some

52   extent by the capillary and surface tension forces of porous materials [15, 16]. However, the

53   lower thermal conductivity of porous materials reduces the heat transfer rate, which has a

54   negative effect on the energy storage efficiency of PCMs composites. Thus far, much research

55   has been done to mix PCMs composites with graphite-based materials, due to excellent thermal

56   conductivity, such as graphite, expanded graphite and carbon nanotubes (CNTs). Tian et al. [17]

57   investigated shaped-stabilized PCMs composites of ternary eutectic chloride/ expanded graphite

58   (EG), and revealed that the thermal conductivities of the composites were 1.35–1.78 times higher

59   than that of the pure ternary eutectic chloride. Mhike et al. [18] attempted to improve the thermal

60   conductivity of PCMs composites by adding graphite and EG. It was found that 10 wt. %

61   graphite and EG showed increases of 60 % and 200 % in thermal conductivity of the PCMs

62 composites, respectively. However, the higher content of graphite reduces the phase change
63 enthalpy of PCMs composites, and the particle-like graphite has no contribution to preventing
64 the leakage problems of the PCMs composites. In addition, Xu et al. [19] have shown that the
65 use of 0.26% MWCNTs can bring clear beneficial effects in improving the thermal conductivity
66 and heat storage/ release rates of the PCMs composites without influencing the chemical
67 compatibility and thermal stability. However, it is still difficult to disperse CNTs uniformly in
68 PCMs composites due to the high surface energy and hydrophobic properties. Therefore, it is
69 very important and urgent to develop an improved method, not only encapsulating the PCMs
70 composites, but also improving the thermal conductivity of the PCMs composites.

71

72 Graphene oxide (GO) is a two-dimensional single layer material with sp^2-bonded carbon atoms,
73 decorated by a large number of covalent oxygen-containing groups-hydroxyl, carbonyl and
74 carboxyl [20]. The exceptional mechanical and thermal properties of GO make it a good
75 candidate for a wide range of applications, such as polymer composite materials, energy storage,
76 biomedical applications and catalysis [21, 22]. It is well known that graphene is a perfect
77 membrane that can completely block the penetration of molecules [23]. Although defects are
78 introduced into the GO structures due to the strong oxidation process, the permeability and
79 thermal conductivity of the GO greatly depends on the oxidation degree and the numbers of
80 layers of the GO. To the best of our knowledge, the well-controlled GO is generally thought to
81 be a perfect material that can prevent the leakage of viscous PCMs and improve the thermal
82 conductivity of the PCMs composites.

83

84 In this study, paraffin and expanded perlite were selected to prepare a EP/PA composite with a
85 high latent heat and a suitable melting temperature for use in buildings, and the GO coating was
86 deposited on the surface of the EP/PA composite. The as-prepared EP/PA/GO composite was
87 composed of paraffin as the core, expanded perlite as the supporting material, and the GO films
88 as the exterior shell. The oxidation degree and the thickness of the GO films deposited on the
89 surface of the EP/PA/GO composite were investigated by X-ray photoelectron spectroscopy
90 (XPS) and typical optical microscopy. The thermal performance of the EP/PA/GO composite was
91 characterized by differential scanning calorimeter (DSC) analysis, thermogravimetric (TGA)
92 analysis and heat storage/release performance tests. The morphology of the EP/PA/GO

93 composite was observed by using a scanning electron microscope (SEM). Chemical

94 compatibility between the paraffin, expanded perlite and GO, was measured by using Fourier

95 transform infrared spectroscopy (FTIR) analysis. The leakage-bearing properties of the

96 EP/PA/GO composite were investigated by a traditional and a newly designed leakage test.

97

98 **2. Experimental**

99 **2.1 Materials**

100 Paraffin in technical grade was supplied by the Ke Qitai Chemical Company, Guangzhou, China.

101 The density and thermal conductivity of the paraffin were 0.81 g/cm^3 and 0.21 W/m·℃,

102 respectively. Expanded perlite was obtained from the Zhongde Perlite Factory, Liaoning, China.

103 The density and mean grain size of the expanded perlite used were 0.31 g/cm^3 and 2-3 mm,

104 respectively. Graphite powder (200 mesh, *99.9995 %, metal basis*) was purchased from Alfa

105 Aesar Inc, Tianjin, China.

106

107 **2.2 Preparation of the GO**

108 GO was prepared from graphite powder (Alfa-Aesar, 200 mesh) according to the modified

109 Hummers' method [24]. Graphite powder (3 g) was added to a solution containing $K_2S_2O_8$ (2 g),

110 P_2O_5 (2 g) and concentrated H_2SO_4 (40 mL, 98 wt. %) for 6 h mixing at 80 °C. The resulting

111 mixture was then diluted with distilled water, filtered and washed until the pH value of the rinse

112 water became neutral. The dried graphite oxide was re-dispersed into concentrated H_2SO_4 (100

113 mL, 98 wt. %) in an ice bath. $KMnO_4$ (15 g) was gradually added and stirred for 2 h. The

114 mixture was then stirred and mixed at 35 °C for another 2 h, followed by the addition of 230 mL

115 of distilled water. The resultant bright yellow solution was terminated by adding 700 mL of

116 distilled water and 15 mL 30% H_2O_2, and subjected to centrifugation and careful washing by

117 37 % HCl and distilled water. After immersing the as-prepared suspension in dialysis tubing

118 cellulose membranes for 7 days, it was finally centrifuged and collected for preparing different

119 concentrations of graphene oxide solution. In this study, the concentration of the GO solution

120 was 2.0 mg/mL.

121

122   **2.3 Preparation of the EP/PA/GO composite**

123   The form-stable EP/PA composite was prepared in the following steps. The mass fraction of

124   paraffin in the EP/PA composite was 0.55 because the homogenous EP/PA composite can be

125   obtained by the direct impregnation method based on our previous research [13]. Firstly, paraffin

126   was melted at a temperature of 50 ºC ± 5 ºC for 1 h in an oven, and then immediately mixed with

127   expanded perlite at ambient temperature and put back in the oven. The mixture was mixed every

128   hour until the paraffin was uniformly dispersed in the expanded perlite. Finally, the form-stable

129   EP/PA composite was formed after cooling down at room temperature. Then, the as-prepared

130   EP/PA composites were added into the GO solution (2 mg/mL) and magnetically stirred for 30

131   min to ensure a uniform dispersion. The resultant mixture was poured into a glass beaker and put

132   into an oven at a temperature of 80 ºC ± 5 ºC for 3 hours . The EP/PA/GO composites were

133   finally fabricated after completing GO solvent evaporation. The color of the as-prepared

134   EP/PA/GO composite changed from white to black due to the successful GO deposition onto the

135   surface of the EP/PA composite, as shown in Fig. 1. The mass fractions of GO in the EP/PA/GO

136   composite were 0.25 wt. % and 0.5 wt. %, and referred to as EP/PA/GO0.25 and EP/PA/GO0.5,

137   respectively.

138

139   **2.4 Characterization**

140   The oxidation degree and the thickness of the GO films were determined by XPS analysis (5600

141   multi-technique system, Physical Electronics) and typical optical microscopy (BX51, Olympus).

142   The thermal performances of the EP/PA/GO composite were characterized by DSC analysis

143   (TAQ 1000) with a heating and cooling rate of 5 °C min under a nitrogen atmosphere. The

144   thermal conductivity the EP/PA/GO composite was verified by comparing the heat

145   storage/release rates of the EP/PA composite with that of the EP/PA/GO composite. The thermal

146   stability of the EP/PA/GO composite was studied by the TGA method (Perkin Elmer) at 10 °C

147   /min under a nitrogen environment. The morphology of the EP/PA/GO composite was observed

148   by using SEM (JEOL, JEM-6390). Chemical compatibility between paraffin, expanded perlite

149   and GO, was measured by FTIR analysis (Bio-Rad FTS 6000). The leakage-bearing properties of

150   the EP/PA/GO composite were investigated by a traditional and a newly designed leakage test.

151

152 **3. Results and discussion**

153 **3.1 DSC analysis of the EP/PA/GO composite**

154 Fig. 2 shows the DSC curves of the EP/PA composite with different GO contents. The detailed

155 thermal results of the measured latent heat (H_M) and the peak phase change temperature (T_{peak})

156 are listed in Table 1. As presented in Fig. 2 and Table 1, the value of T_{peak} in the melting and

157 freezing processes were determined as 50.72 °C and 42.54 °C for the EP/PA composite, and

158 50.86 °C and 42.22 °C for the EP/PA/GO0.25 composite, and 50.96 °C and 42.14 °C for the

159 EP/PA/GO0.5 composite. The results indicate that the GO incorporation does not cause a shift of

160 the peak phase change temperature of the EP/PA composite. Moreover, the value of H_M in the

161 melting and freezing processes were 80.92 J/g and 80.48 J/g for the EP/PA composite, 80.16 J/g

162 and 80.21 J/g for the EP/PA/GO0.25 composite and 79.75 J/g and 79.36 J/g for the EP/PA/GO0.5

163 composite. It clearly can be seen that the EP/PA composite, with and without the GO, shows an

164 almost equivalent latent heat capacity and low latent heat capacity loss resulting from the small

165 loading of GO incorporation, within 0.5 wt. %. Therefore, it can be concluded that 0.5 wt. % GO

166 leads to a trivial change of the values of H_M and T_{peak} of the EP/PA composite, and that the

167 EP/PA/GO composite can be effectively used as an energy storage material for exterior walls in

168 building applications.

169

170 **Table 1** Thermal properties of the EP/PA composite with different content of the GO.

171

Composite	Melting Process		Freezing Process	
	T_{peak}	H_M	T_{peak}	H_M
	(ºC)	(J/g)	(ºC)	(J/g)
EP/PA	50.72	80.92	42.54	80.84
EP/PA/GO0.25	50.86	80.16	42.22	80.21
EP/PA/GO0.5	50.96	79.75	42.14	79.36

172

173

174 **3.2 Thermal stability of the EP/PA/GO composite**

175   The thermal stability of the EP/PA composite with different GO contents was evaluated by TGA

176   analysis. Fig. 3 shows the measured TGA curves of the EP/PA composite, the EP/PA/GO0.25

177   composite and the EP/PA/GO0.5 composite. As shown in Fig. 3, the EP/PA composite starts to

178   lose weight at approximately 105 °C. After rapid weight loss due to paraffin evaporation, there is

179   a loss of 55.24 % of the paraffin weight at 360 °C, which is almost consistent with the design

180   mix proportion of the expanded perlite and paraffin, indicating that the EP/PA composite is

181   homogeneous. With the incorporation of the GO, there are no obvious changes in the starting

182   decomposition temperature and the weight loss rate the EP/PA/GO composite. The only

183   differences, by comparing the three curves in Fig. 3, are the final weight loss of the different

184   composites. Compared with the weight loss of the EP/PA composite (55.24 %), it slightly

185   increases to 55.50 % and 55.82 % for the EP/PA/GO0.25 composite and the EP/PA/GO0.5

186   composite, respectively. The negligible change is attributed to the small GO loading, up to 0.5

187   wt. %. In addition, no decomposition is seen for all the composites over their phase change

188   temperature ranges, showing the good thermal stability of the EP/PA/GO composite.

189

190   **3.3 Thermal conductivity of the EP/PA/GO composite**

191   Thermal conductivity is a key parameter to determine the thermal storage performance of PCMs

192   composites. The heat storage/release performance of the EP/PA/GO composite was investigated

193   by using the test setup schematically shown in Fig. 4 [19]. In this test, 5 g of the PCMs

194   composite was stored in a sealed tube. Two water baths, at temperatures of 60 °C and 30 °C,

195   were adopted during the heating storage/release processes. The temperature change of the PCMs

196   composite during the heating storage/release test was measured by thermocouples located in the

197   middle of the PCMs composite stack in the sealed tube and recorded through a data-logger and a

198   computer.

199

200   Fig. 5 shows the temperature curves for melting and freezing of the EP/PA composite with

201   different GO mass fractions in the heat storage/release performance tests. Table 2 lists the time

202   taken for temperatures increasing from 30 ºC to 60 ºC and decreasing from 60 ºC to 30 ºC. The

203   shorter the time, the faster the heat storage and release rate, and the higher the thermal

204   conductivity of the composite. As shown in Fig. 5 and Table 2, all the composites have obvious

205   temperature plateaus in the heating and cooling processes due to the occurrence of phase

206 changes. In detail, when temperature increases from 30 ºC to 60 ºC, it takes 8.8 min, 6.2 min and

207 4.1 min for the EP/PA composite, the EP/PA/GO0.25 composite and the EP/PA/GO0.5,

208 respectively. Similarly, it takes 14.2 min, 11.8 min and 7.5 min for each composite when the

209 temperature decreases from 60 ºC to 30 ºC. It clearly shows that the time used for both the

210 melting and freezing processes decreases with the increasing content of GO within 0.5 wt. %,

211 and the EP/PA/GO0.25 and EP/PA/GO0.5 composites show clearly faster heat storage and

212 release rates than the EP/PA composite. The experimental results indicate that the EP/PA/GO0.5

213 composite has 2 times faster heat storage/release rates compared to that of the EP/PA composite

214 due to the enhanced thermal conductivity. The significant improvement is much better than many

215 other studies reported. For example, Li et al. [19] demonstrated that 0.26 wt. % CNTs led to 1.25

216 times faster heat storage/release rates for paraffin/diatomite composites; however, uniform

217 dispersion of CNTs in the PCMs composite is difficult to accomplish. Liu et al. [25] have shown

218 that the time required in heat storage/release tests was reduced by 3 times with the addition of 1

219 wt. % graphite; however, the latent heat loss of the composite decreased significantly due to the

220 higher loading of the graphite, and the leakage problem still could not be avoided by the addition

221 of graphite. In this study, 0.5 wt. % GO incorporation not only reduces the time required in heat

222 storage/release tests by a factor of 2, but also keeps the latent heat capacity of the PCMs

223 composite stable. Therefore, GO has a great influence on improving the thermal properties of the

224 EP/PA composite.

225

226   Table 2 Time for heating and cooling of EP/PA composite with different GO content

Composite Temperature range	EP/PA	EP/PA/GO0.25	EP/PA/GO0.5
30 °C -60 °C	8.8 min	6.2 min	4.1 min
60 °C -30 °C	14.2 min	11.8 min	7.5 min

227

228 **3.4 Chemical compatibility of the EP/PA/GO composite**

229 Fig. 6 shows the FTIR spectrums of the EP/PA composite with different GO contents. As

230 presented in Fig. 6, the characteristic peaks of the GO at 1723 cm^{-1}, 1621 cm^{-1}, 1222 cm^{-1} and

231 1058 cm^{-1} indicate carboxyl or carbonyl C=O stretching, H-O-H bending band of the absorbed

232 H_2O molecules, phenolic C-OH stretching and alkoxy C-O stretching, respectively. Moreover,

233   the EP/PA composite has six characteristic absorption bands: skeleton vibration of C-C at 455

234   cm^{-1}, rocking vibration of $-CH_2$ at 718 cm^{-1}, two deformation vibrations of $-CH_2$ and $-CH_3$ at

235   1368 cm^{-1} and 1468 cm^{-1}, and two stretching vibrations of $-CH_2$ and $-CH_3$ at 2848 cm^{-1} and 2917

236   cm^{-1}, respectively. It is clearly seen that all the above-mentioned characteristic absorption bands

237   of the GO and the EP/PA composite are included in the FTIR spectrums of the EP/PA/GO0.5

238   composite. More importantly, no new characteristic absorption bands are generated in the FTIR

239   spectrums of the EP/PA/GO0.5 composite, suggesting that there is no chemical reaction between

240   the GO and the EP/PA composite. Therefore, it can be concluded that the EP/PA/GO composite

241   has a good chemical compatibility.

242

3.5 Leakage-bearing properties of the EP/PA/GO composite

244   Fig. 7 shows the SEM images of the surface morphologies of the expanded perlite, the EP/PA

245   composite and the EP/PA/GO composite. As seen from Fig. 7a, the expanded perlite has a highly

246   porous structure, which makes it a good supporting material to absorb molten paraffin. Fig. 7b

247   shows that the paraffin is uniformly absorbed into the pores of the expanded perlite, and hence

248   the leakage of the molten paraffin from the composites is largely prevente. Fig. 7c shows the GO

249   coating on the surface of the EP/PA composite. It is clear that the pores of the EP/PA composite

250   are encapsulated with the GO coating, which acts like a shell to prevent the molten paraffin

251   leaking out. However, whether the molten paraffin can permeate the GO coating makes a great

252   influence on the leakage-bearing properties of the EP/PA/GO composite. In order to verify this

253   point, leakage testing for the GO films was conducted, as shown in Fig. 8. The GO film was

254   obtained from the GO solution (the dosage and concentration equivalent to that used for the

255   fabrication of the EP/PA/GO0.5 composite) by an oven drying method, and then placed into the

256   middle of the suction device (Fig. 8). The lamp was turned on to ensure that the paraffin was in a

257   molten condition during the leakage test. The experimental results showed that there is no molten

258   paraffin penetrated though the GO films to the bottom conical flask after 24 h heating, which

259   confirms that the GO films are effective in preventing the leakage of the molten paraffin.

260   Moreover, the traditional leakage test was carried under condition in which the EP/PA composite

261   and the EP/PA/GO0.5 composite were put on a filter and placed under the lamp, as seen in Fig.

262   9. The distance between the lamp and the composite was 10 cm to ensure that all the paraffin

263   could melt and solidify in the thermal cycling test with 3 min of lamp 'on' and 9 min of lamp

264   'off'. The experimental results revealed that there was no paraffin trace on the filter for the

265   EP/PA composite and the EP/PA/GO0.5 composite after 1500 thermal cycles, because the molten

266   paraffin could be limited in the pores of the expanded perlite by the capillary and surface tension

267   forces. However, after 3000 cycling, a small amount of paraffin was observed on the filter for the

268   EP/PA composite, caused by the paraffin leakage, but there was no paraffin trace on the filter for

269   the EP/PA/GO0.5 composite, as seen in Fig. 10c and 10f. The possible reason is that the GO

270   coating on the surface of the EP/PA/GO0.5 composite contributes to preventing the molten

271   paraffin leakage, which is consistent with the previous results as seen in Fig. 8. It also indicates

272   that the leakage protection for the molten paraffin, caused by the capillary and surface tension

273   forces of the expanded perlite, is good for short term use; however, the EP/PA composite covered

274   with GO coating shows an excellent leakage-bearing property, which has great potential for use

275   in energy efficient buildings for long term consideration.

276

277   Since the permeability of the GO coating greatly depends on the thickness and the oxidation

278   degree of the GO layers, the cross-section of the EP/PA/GO0.5 composite was examined by an

279   optical microscopy to measure the thickness of the GO coating, and the XPS test was carried out

280   to investigate the oxidation degree of the GO. Fig. 11a shows the cross-sectional image of the

281   EP/PA/GO0.5 composite. It is clear that the surface of the composite is uniformly covered by the

282   GO films, and the thickness of the GO films is about 50 μm. Fig. 11b shows the XPS spectra of

283   the GO used in this study, and the deconvoluted C1s XPS spectra of the GO, clearly shows four

284   types of carbon bonds, including the C-C at 284.5 eV, C-O at 286.4 eV, C=O 288.3 at eV and -

285   COOH at 289.0 eV. The elemental analysis of the XPS results indicate that the C/O ratio and

286   oxygen content of the GO in this study are 3.0 and 30.7 %, respectively. Therefore, it can be

287   concluded that the GO films with a C/O ratio of 3.0 and thickness of 50 μm, in this study, can

288   effectively prevent the leakage problem of the EP/PA composite for long term use. However, it

289   should be noted that the leakage-bearing properties of the EP/PA/GO composite greatly depends

290   on the oxidation degree and the thickness of the GO films. A greater oxidation degree or less

291   thickness of the GO films might cause negative effects on the leakage-bearing properties of the

292   EP/PA/GO composite.

293

4. Conclusions

In this study, a novel phase change material of expanded perlite/paraffin/graphene oxide (EP/PA/GO) with enhanced thermal properties was fabricated by depositing GO films on the surface of the EP/PA composite. The DSC and TGA results showed that the EP/PA/GO composites had small latent heat capacity and weight losses due to the small loading of the GO incorporation, within 0.5 wt. %. The FTIR results indicated that the EP/PA/GO composite had good chemical compatibility. In addition, due to the excellent thermal conductivity of the GO, the heat storage/release performance test results showed that the EP/PA/GO0.5 composite had 2 times faster heat storage/release rates compared to that of the EP/PA composite. More importantly, the GO films covering the surface of the EP/PA composite can greatly prevent the leakage problems of molten paraffin. No leakage of paraffin occurred after thermal cycling 3000 times. Therefore, the EP/PA/GO composites have shown a great potential for thermal energy storage applications due to the enhanced thermal properties, good leakage-bearing properties and excellent chemical compatibility.

References

[1] Kalogirou SA, Florides G, Tassou S. Energy analysis of buildings employing thermal mass in Cyprus. Renewable Energy. 2002;27(3):353-68.
[2] Bojić M, Miletić M, Bojić L. Optimization of thermal insulation to achieve energy savings in low energy house (refurbishment). Energy Conversion and Management. 2014;84:681-90.
[3] Kalogirou SA, Karellas S, Badescu V, Braimakis K. Exergy analysis on solar thermal systems: A better understanding of their sustainability. Renewable Energy. 2015.
[4] Şahan N, Fois M, Paksoy H. Improving thermal conductivity phase change materials—A study of paraffin nanomagnetite composites. Solar Energy Materials and Solar Cells. 2015;137:61-7.
[5] Kalogirou SA. Solar thermal collectors and applications. Progress in energy and combustion science. 2004;30(3):231-95.

328   [6]   Song S, Dong L, Zhang Y, Chen S, Li Q, Guo Y, et al. Lauric acid/intercalated kaolinite
329   as form-stable phase change material for thermal energy storage. Energy. 2014;76:385-9.
330   [7]   Chung O, Jeong S-G, Kim S. Preparation of energy efficient paraffinic PCMs/expanded
331   vermiculite and perlite composites for energy saving in buildings. Solar Energy Materials and
332   Solar Cells. 2015;137:107-12.
333   [8]   Zhang Y, Zheng X, Wang H, Du Q. Encapsulated phase change materials stabilized by
334   modified graphene oxide. Journal of Materials Chemistry A. 2014;2(15):5304-14.
335   [9]   Chen Z, Wang J, Yu F, Zhang Z, Gao X. Preparation and properties of graphene oxide-
336   modified poly (melamine-formaldehyde) microcapsules containing phase change material n-
337   dodecanol for thermal energy storage. Journal of Materials Chemistry A. 2015;3(21):11624-30.
338   [10]   Fu X, Liu Z, Xiao Y, Wang J, Lei J. Preparation and properties of lauric acid/diatomite
339   composites as novel form-stable phase change materials for thermal energy storage. Energy and
340   Buildings. 2015.
341   [11]   Li X, Sanjayan JG, Wilson JL. Fabrication and stability of form-stable diatomite/paraffin
342   phase change material composites. Energy and Buildings. 2014;76:284-94.
343   [12]   Zhang J, Guan X, Song X, Hou H, Yang Z, Zhu J. Preparation and properties of gypsum
344   based energy storage materials with capric acid–palmitic acid/expanded perlite composite PCM.
345   Energy and Buildings. 2015;92:155-60.
346   [13]   Lu Z, Xu B, Zhang J, Zhu Y, Sun G, Li Z. Preparation and characterization of expanded
347   perlite/paraffin composite as form-stable phase change material. Solar Energy. 2014;108:460-6.
348   [14]   Lu Z, Zhang J, Sun G, Xu B, Li Z, Gong C. Effects of the form-stable expanded
349   perlite/paraffin composite on cement manufactured by extrusion technique. Energy. 2015.
350   [15]   Yuan Y, Yuan Y, Zhang N, Du Y, Cao X. Preparation and thermal characterization of
351   capric–myristic–palmitic acid/expanded graphite composite as phase change material for energy
352   storage. Materials Letters. 2014;125:154-7.
353   [16]   Wang S, Qin P, Fang X, Zhang Z, Wang S, Liu X. A novel sebacic acid/expanded graphite
354   composite phase change material for solar thermal medium-temperature applications. Solar
355   Energy. 2014;99:283-90.
356   [17]   Tian H, Wang W, Ding J, Wei X, Song M, Yang J. Thermal conductivities and
357   characteristics of ternary eutectic chloride/expanded graphite thermal energy storage composites.
358   Applied Energy. 2015;148:87-92.
359   [18]   Mhike W, Focke WW, Mofokeng J, Luyt AS. Thermally conductive phase-change
360   materials for energy storage based on low-density polyethylene, soft Fischer–Tropsch wax and
361   graphite. Thermochimica Acta. 2012;527:75-82.
362   [19]   Xu B, Li Z. Paraffin/diatomite/multi-wall carbon nanotubes composite phase change
363   material tailor-made for thermal energy storage cement-based composites. Energy. 2014;72:371-
364   80.
365   [20]   Ramadoss A, Saravanakumar B, Kim SJ. Thermally Reduced Graphene Oxide-coated
366   Fabrics for Flexible Supercapacitors and Self-powered Systems. Nano Energy. 2015.
367   [21]   Wang Z, Liu C-J. Preparation and application of iron oxide/graphene based composites
368   for electrochemical energy storage and energy conversion devices: Current status and
369   perspective. Nano Energy. 2015;11:277-93.
370   [22]   Yang H, Lee D, Park K, Kim W. Platinum–boron doped graphene intercalated by carbon
371   black for cathode catalyst in proton exchange membrane fuel cell. Energy. 2015.
372   [23]   Tsetseris L, Pantelides S. Graphene: An impermeable or selectively permeable membrane
373   for atomic species? Carbon. 2014;67:58-63.

374 [24]   Hummers Jr WS, Offeman RE. Preparation of graphitic oxide. Journal of the American
375 Chemical Society. 1958;80(6):1339-.
376 [25]   Liu C, Yuan Y, Zhang N, Cao X, Yang X. A novel PCM of lauric–myristic–stearic
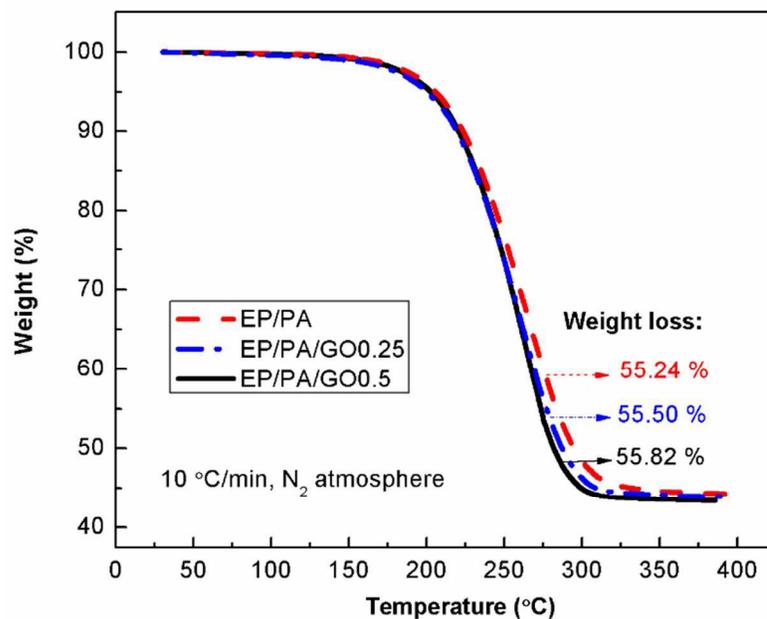377 acid/expanded graphite composite for thermal energy storage. Materials Letters. 2014;120:43-6.
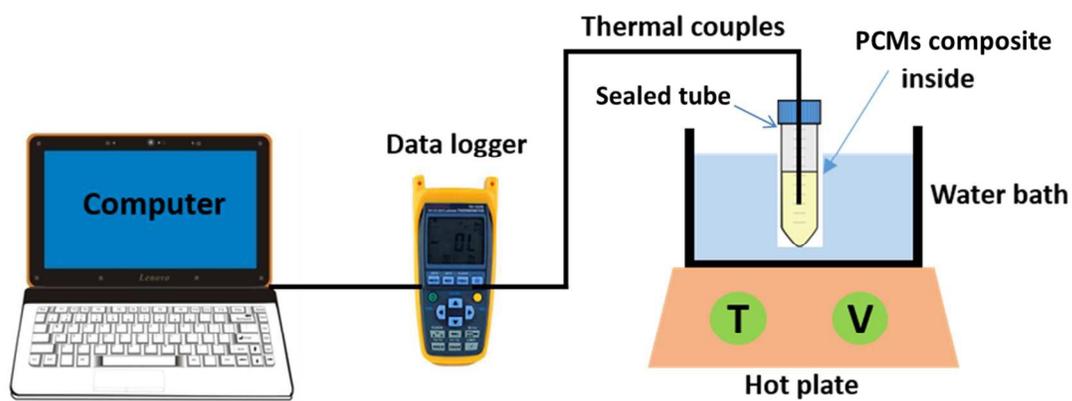378

Figures Captions

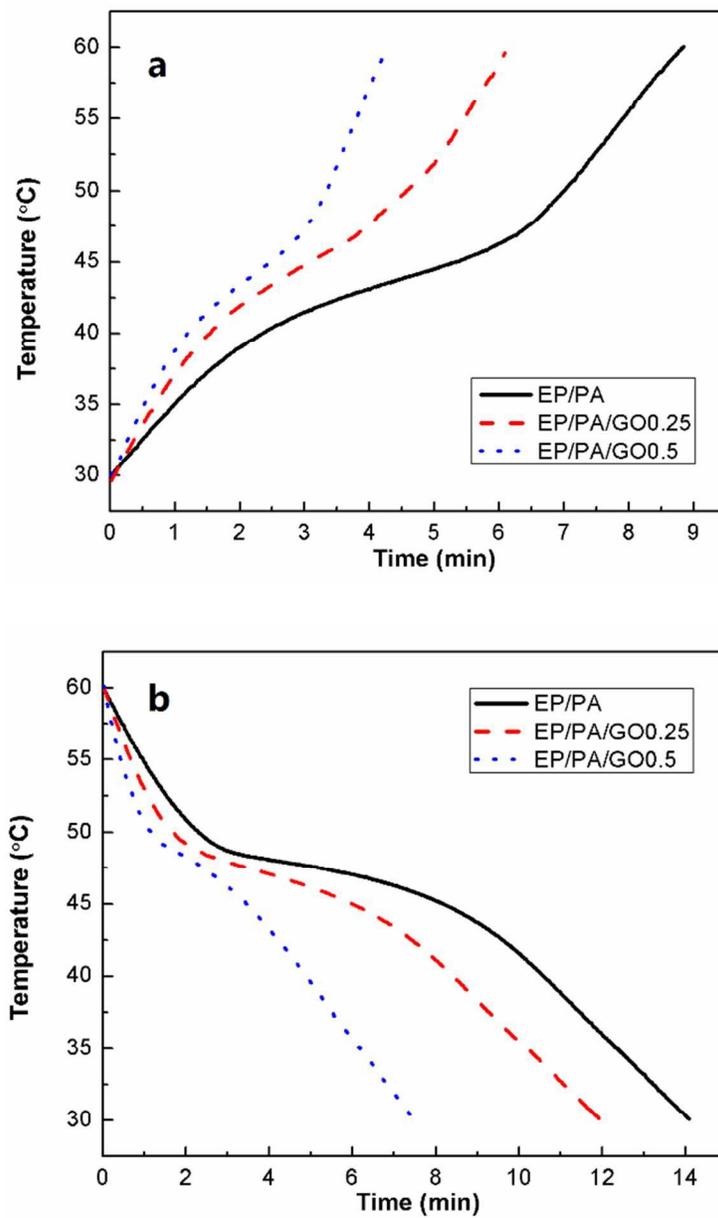**Fig. 1.** Image of the EP/PA composite and the EP/PA/GO0.5 composite.

Fig. 2. DSC curves of the EP/PA composite with different GO contents.
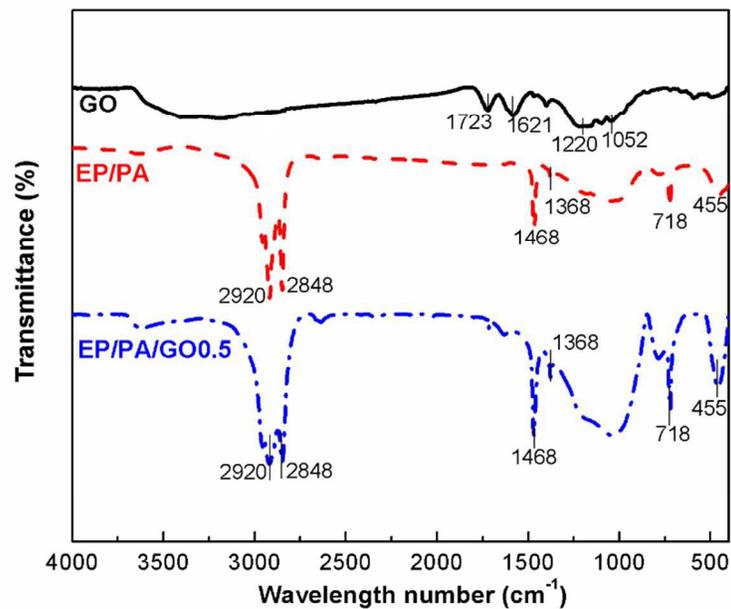
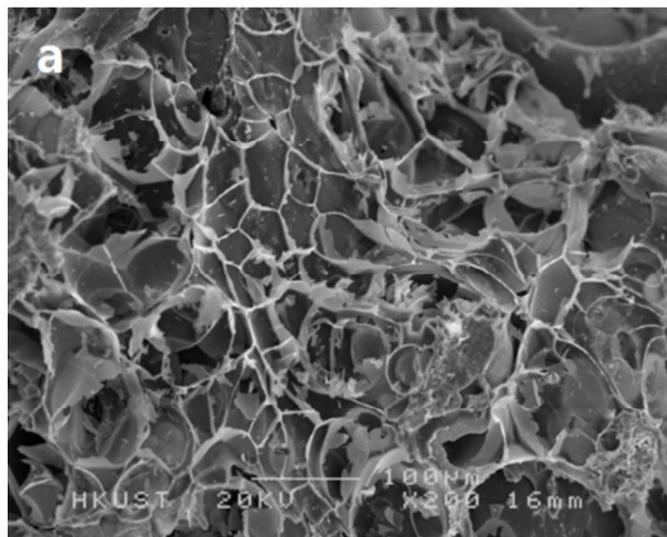**Fig. 3.** TGA curves of the EP/PA composite with different GO contents.

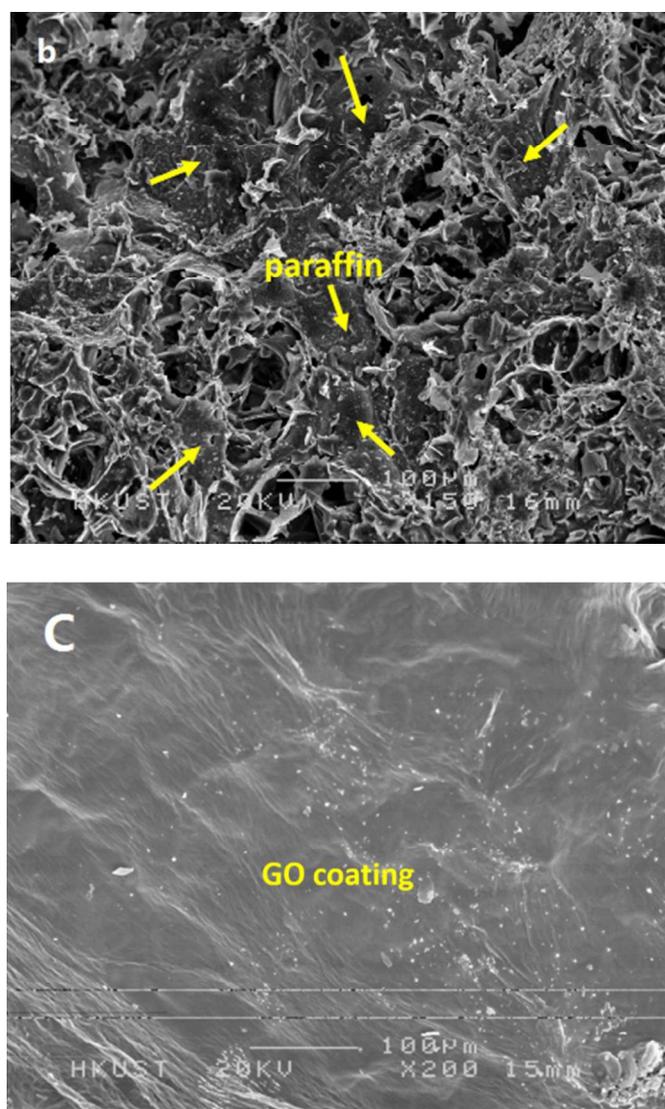**Fig. 4.** Schematic diagram of heat storage/release performance test.

Fig. 5. Melting (a) and freezing (b) curves of the EP/PA composite, the EP/PA/GO0.25 composite and the EP/PA/GO0.5 composite.
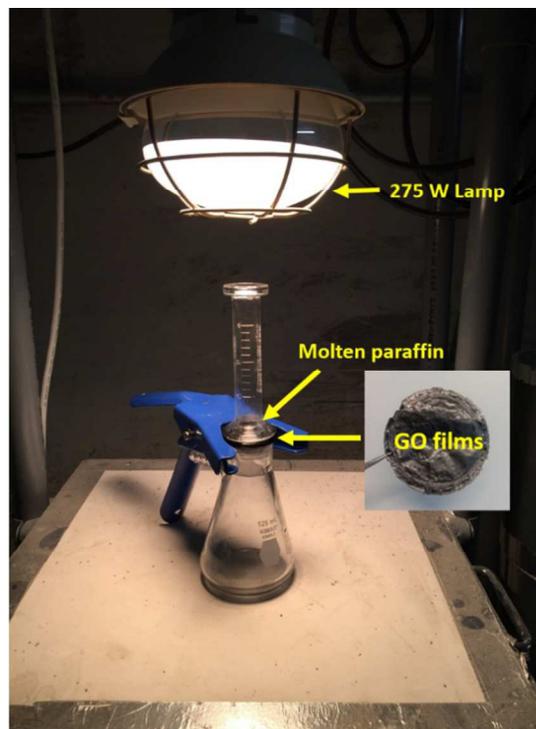
Fig. 6. FTIR curves of the GO, EP/PA composite and EP/PA/GO0.5 composite.

Fig. 7. The surface morphologies of (a) the expanded perlite, (b) the EP/PA composite and (c) the EP/PA/GO0.5 composite.

Fig. 8. Leakage test for the GO films.

Fig. 9. Thermal cycling test.

Fig. 10. Leakage test for the EP/PA composite (a) before thermal cycling test (b) after 1500 cycling (c) after 3000 cycling; the EP/PA/GO0.5 composite (d) before thermal cycling test (e) after 1500 cycling (f) after 3000 cycling.

Fig. 11. (a) Cross-section image of the EP/PA/GO0.5 composite; (b) XPS spectra of the GO.

Figures

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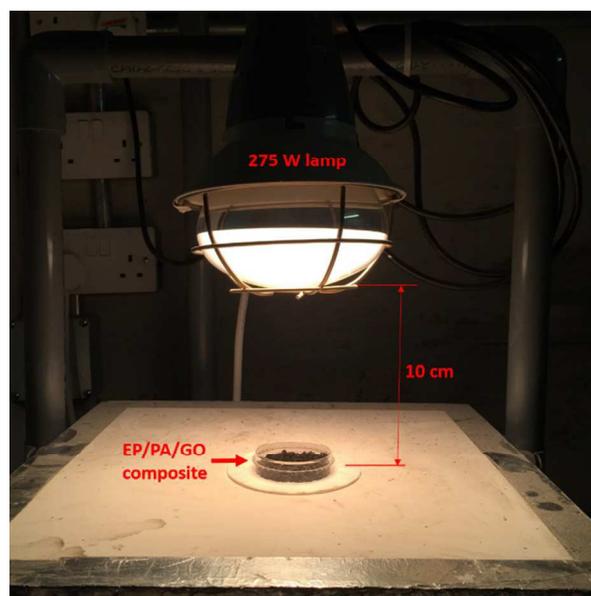**Fig. 6.** FTIR curves of the GO, EP/PA composite and EP/PA/GO0.5 composite.
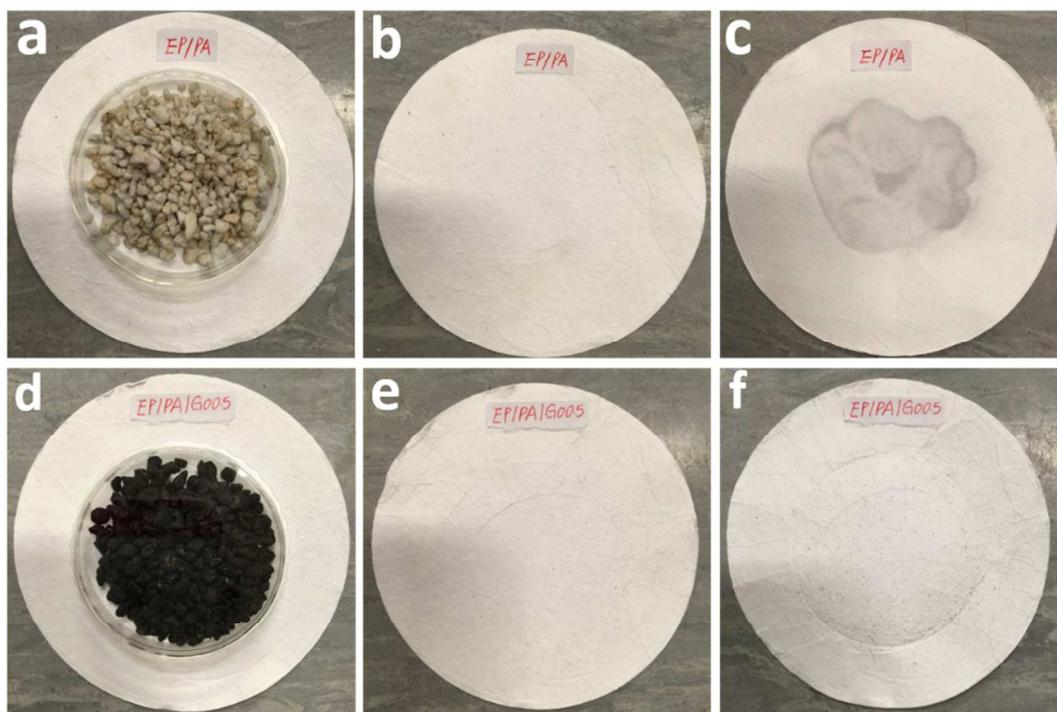
Fig. 7. The surface morphologies of (a) the expanded perlite, (b) the EP/PA composite and (c) the EP/PA/GO0.5 composite.
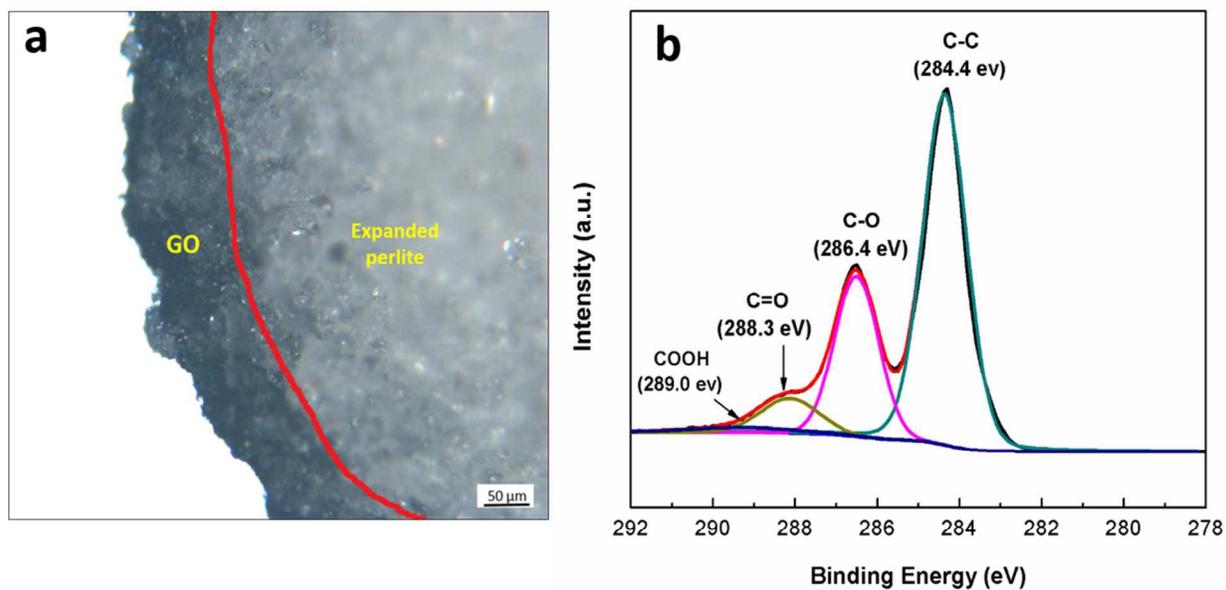
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