

1 Encapsulation of phase change materials using rice-husk-char

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13

14 **ABSTRACT**

15 This paper explored a new approach to prepare phase change microcapsules using carbon-based
16 particles via Pickering emulsions for energy storage applications. A rice-husk-char, a by-product
17 in biofuel production, containing 53.58 wt% of Carbon was used as a model carbon-based material
18 to encapsulate hexadecane, a model phase change material. Hexadecane was emulsified in aqueous
19 suspensions of rice-husk-char nanoparticles. Water soluble polymers poly(diallyldimethyl-
20 ammonium chloride) and poly(sodium styrene sulfonate) were used to fix the rice-husk-char
21 nanoparticles on the emulsion droplets through layer-by-layer assembly to enhance the structural
22 stability of the microcapsules. The microcapsules formed are composed of a thin shell
23 encompassing a large core consisting of hexadecane. Thermal gravimetric and differential
24 scanning calorimeter analyses showed the phase change enthalpy of 80.9 kJ kg⁻¹ or 120.0 MJ m⁻³.
25 Design criteria of phase change microcapsules and preparation considerations were discussed in
26 terms of desired applications. This work demonstrated possible utilisations of biomass-originated
27 carbon-based material for thermal energy recovery and storage applications, which can be a new
28 route of carbon capture and utilisation.

29 **Keywords:** Thermal energy storage, phase change microcapsules, rice husk char, Pickering
30 emulsion, layer-by-layer assembly

31 **1. INTRODUCTION**

32 Energy consumed for low and intermediate rank heat accounts for ~ 90% of energy consumption
33 in industrial and household applications [1]. A large proportion of the heat is discharged into the

34 environment through undesired heat loss in maintaining temperatures. In order to reduce the overall
35 energy consumption and CO₂ emission worldwide, cost-effective thermal systems have been under
36 development to reduce the heat loss and to harvest solar energy and store it as heat for reuse [2,
37 3]. Thermal media is a key to effective thermal systems. In general, the desired thermal media
38 should have (a) a high dynamic thermal energy density; (b) long term stability and (c) low cost for
39 economic sustainability and (d) excellent flow and heat transportation properties (if in the form of
40 working fluids). Phase change material slurries have been developed to serve as thermal fluids for
41 both heat transfer and energy storage [2, 3], where the phase change materials encapsulated are
42 dispersed in an immiscible liquid carrier in order to maintain the fluidity of the media during phase
43 changes. In this way, the phase change material slurries have higher heat density at points around
44 the phase change temperature and also the desired fluidity.

45 Active research into phase change microcapsules by experiments and simulations in different
46 thermal systems are reviewed in references [3, 4]. Different results were observed in relation to
47 application scenarios. The well-known Micronal® phase change microcapsules were
48 commercialised, which can be incorporated in interior walls of buildings for intelligent
49 temperature management. Its enhancement in energy efficiency has been well approved in the
50 stagnant environment for a low frequency heat charge and discharge [5, 6], but its economic
51 efficiency has been questioned. In laminar or transient flow regions, heat transfer enhancements
52 can be spotted clearly in heat pumps [7]. While enhancements are less significant in more intense
53 processing environments such as solar heat harvest and release due to slow heat transfer rates [8,
54 9].

55 Critical analysis has shown that polymers such as poly(methyl methacrylate) such as poly(methyl
56 methacrylate) [10, 11], poly(melamiformaldehyde) [4, 12], poly urea and (urea formaldehyde) [4,
57 12], polystyrene [13] and polyethylene [14] are common encapsulates studied for phase change
58 microcapsules. These polymers inherently have low thermal conductivities ($\sim 0.25 \text{ W m}^{-1}\text{K}^{-1}$) and
59 low densities, hence slow heat capture and release rates and limited volumetric heat densities. In
60 recent years, inorganic materials including metal, metal oxides, insoluble salts and carbon-based
61 materials (graphene and carbon nanotube) have been used in the modification of the microcapsule
62 shell by coating or as additives for enhancing their thermal conductivity. Microcapsules with silver
63 coating as the second layer [15, 16], hybrid magnetic Fe₃O₄/SiO₂ [17], silicon nitride powder-
64 modified polymethylmethacrylate [18] and calcium carbonate shells [19] have all displayed
65 significant improvements in thermal conductivity.

66 Carbon-based materials varying from diamond, graphite (carbon fibre), carbon nanotubes and
67 graphene to amorphous carbons are well known for their wide range of thermal conductivities (~ 21
68 - $5000 \text{ W m}^{-1}\cdot\text{K}^{-1}$). The addition of 20 wt% expanded graphite in paraffin results in a 7.5 fold
69 thermal conductivity increase for the formation of a carbon network structure [20]. As an example
70 composite panels consisting of phase change materials and expanded graphite (ECOPHIT®)
71 installed as radiant ceilings at the Deutsche Bank headquarters demonstrated a 67 % reduction in
72 energy use for heating and cooling [21, 22]. Both the heat storage capacity of the phase change
73 materials and the high thermal conductivity of graphite sheets contributed to the result. Phase
74 change microcapsules of urea–formaldehyde resin with 4% of carbon nanotubes showed an
75 increase in thermal conductivity by 79.2% compared with that without carbon nanotubes [23].
76 These results inspire researchers to develop carbon-based phase change microcapsules aiming at
77 achieving large heat capacities and high heat transfer rates as desired properties.

78 Using carbon-based materials as microcapsule shells their absolute thermal conductivity is
79 expected to be higher than that of polymer nanocomposites containing a small fraction of carbon
80 nanotubes [23-25]. However, high thermal conductive carbon materials can form only at high
81 temperatures, typically above 600°C , which is much higher than the decomposition temperature
82 of organic carbon-carbon bonds. As a result, it is very difficult to grow thermally conductive
83 carbon on the surface of phase change “droplets”. Fortunately, solid particles can be directly used
84 to manufacture microcapsules through a Pickering emulsion, which is the emulsion using solid
85 particles as emulsifier [26]. All the carbon materials mentioned above are available as solid micro-
86 or nanoparticles.

87 Pickering emulsion droplets are formed by the adsorption of one monolayer of solid particles on
88 the droplet surface, thus generating core-shell structures [27, 28]. Many different types of
89 inorganic nanoparticles such as silica [26-28], metal organic framework nanoparticles [29, 30] and
90 carbon nanotubes [31] have been successfully incorporated in stabilising Pickering emulsions
91 either as a single emulsifier or co-emulsifier [32], among which silica nanoparticles have been
92 more extensively studied. For example, Ding *et. al.* prepared structured microcapsules using silica
93 nanoparticles that are formed in-situ by the hydrolysis of methyl trimethoxysilane and 3-
94 aminopropyl trimethoxysilane [28]. The prepared microcapsules contained a significant core of *n*-
95 octodecane, a phase change material, with a monolayer of silica nanoparticles as shell giving a
96 high volumetric encapsulation ratio of 65 wt%. The nanoparticles can be manipulated for the
97 desired arrangement on the droplet surface through tailoring size, shape, surface chemistry and
98 adsorption kinetics [32]. Pickering emulsions, in particular those stabilised by latex nanoparticles,

99 have been successfully encapsulated by polymer melting [33, 34], cross-linking from the inside
100 [27] or outside of microcapsules. The microcapsule wall formed has been tailored to have a
101 different permeability from vapour-proof to highly porous with desired pore sizes [27, 28, 34].
102 This knowledge stimulated our study of using carbon-based particles to produce phase change
103 microcapsules.

104 The model carbon-based material used in this study is rice-husk-char, which is rich in carbon and
105 silica [35, 36]. It is an abundant by-product in countries which produce and consume rice. Up to
106 now, there are insufficient applications of rice-husk-char to support a sustainable consumption
107 chain. This study proposes its use in the development of new applications of carbon-based
108 materials for thermal energy storage in civil engineering.

109 Rice husk char used in this study was obtained from slow pyrolysis for bio-oil production. After
110 milling down to desired sizes the rice husk char particles were dispersed in water to be used as a
111 solid emulsifier in the stabilisation of phase change material emulsion. The emulsion droplets were
112 then subjected to a layer by layer assembly of polyelectrolyte chains in an aqueous solution for
113 encapsulation. Following this, thermogravimetric and differential scanning calorimetric analyses
114 were carried out on the microcapsules produced in order to assess their thermal stability and heat
115 storage capacity.

116

117 **2. EXPERIMENTAL**

118 **2.1 Materials**

119 n-Hexadecane (99%, Acros Organics) was used as a model phase change material to be
120 encapsulated for a phase change at around 20°C to be used in a living environment. The rice husk
121 char was used as a Pickering emulsion stabiliser and also as the wall construction material of the
122 n-hexadecane microcapsule. The char was made from the slow pyrolysis of Brunei rice husk at
123 450°C for 30 minutes in the presence of nitrogen gas [37], which generated 42 wt% of char based
124 on dry rice husk.

125 Poly (diallyldimethylammonium chloride) (PDADMAC 20 wt% aq., 400k-500k g mol⁻¹, Sigma
126 Aldrich) and poly (sodium styrene sulfonate) (PSS 30 wt% aq., 200k g mol⁻¹, Sigma Aldrich) were
127 used as negatively and positively charged polymers, respectively, for layer-by-layer adsorption to
128 fix the rice husk char particles on the emulsion droplets. Sunflower oil (Tesco UK) was used as an
129 osmosis additive to the oil phase for better size and stability control in emulsification. Deionised
130 water was used in all the sample preparation.

131 **2.2 Sizing of the rice husk char**

132 The rice husk char received from the pyrolysis was ground dry in air using a planetary ball mill
133 (Fritsch Pulverisette 6). The milling used a 250 ml zirconia grinding bowl and zirconia milling
134 balls (1mm in diameter) of 200 g, and was carried out at 6000 rpm for 5 minutes to size down the
135 rice husk char down to a nanometer range. The rice husk char (RHC) nanoparticles were analysed
136 using laser scattering for its particle size and size distribution, and dynamic laser scattering for its
137 surface charge measured as zeta potential. The RHC nanoparticle sample prepared dry in air was
138 dispersed in deionised water to give aqueous suspensions with a concentration in the range of 0.5
139 - 2.0 wt%. The suspensions were used as the continuous phase in the emulsification of n-
140 hexadecane.

141 **2.3 Emulsification and encapsulation**

142 For a typical emulsification operation, 1 ml of n-hexadecane and 3 ml of RHC suspension was
143 homogenised at 10-20k rpm using a rotor-stator homogeniser (Kinematica Polytron PT2500E) for
144 a specified time (2-5 minutes) at room temperatures. The emulsion droplets were sampled on a
145 glass slide and examined using an optical microscope for droplet size and size distribution, and
146 preliminarily for the RHC nanoparticles adsorption on the oil droplet.

147 For encapsulation, 1 ml of droplet sample was carefully added into 10 ml of aqueous solution of
148 PDADMAC with a concentration of 2.0 wt% or 5.0 wt%. The mixture was gently shaken/stirred
149 for 24 hours to allow the adsorption completion. The PDADMAC adsorbed droplet was then
150 subjected to the adsorption of PSS (10.0 mL 5.0 wt% PSS) following the same operation procedure.

151 Samples were taken at the end of each coating operation and examined using an optical microscope.
152 The product was then dried naturally in air at a room temperature for 2 weeks, where the relative
153 humidity was ~35-38%. The dried sample was analysed using a thermogravimetric analyser and
154 differential scanning calorimetry.

155 **2.4 Characterisation**

156 Attenuated Total Reflection (ATR) is used to measure the infrared spectroscopy of the RHC
157 sample (Bruker Optics' ALPHA). The measurement was carried out in the wavelength range from
158 400 to 4000 cm^{-1} and the spectroscopy reported is the average of 64 scans to ensure the reliability
159 of data collected.

160

161 The sizes and surface zeta potential of the RHC particle was characterised by laser scattering
 162 (Molvern HPPS, Nanoziser). A Motic BA310 Digital Biological Microscope with an objective
 163 lens of 4x, 10x, 40x and 100x was used for the examination of RHC particle stabilised droplets.
 164 The size measurement was calibrated using the microbar provided by Motic.

165
 166 Thermogravimetric Analysis (TGA) was performed using a Perkin Elmer Pyris 1. A sample of 5 -
 167 10mg was heated from room temperature to 600 °C at a heating rate of 10 °C /minute in the flow
 168 of nitrogen (purity > 99%) at 30 ml/minute. The nitrogen was generated by an in-house adsorber.
 169 The differential scanning calorimetric (DSC) diagrams were recorded using a METTLER
 170 TOLEDO DSC1 in the temperature range from -50 to 50°C. Samples of 5-10mg were placed in
 171 aluminium pans. Both the heating and cooling rates were maintained at 10°C /minute using liquid
 172 nitrogen and nitrogen gas as the purging and protective gas. The specific melting heat of the phase
 173 change microcapsule measured was used for the calculation of encapsulation ratio of the phase
 174 change material by comparing with the specific melting heat of the pure phase change material
 175 using the following equation.

$$\text{Encapsulation ratio} = \frac{\text{Specific melting heat of microcapsule sample}}{\text{Specific melting heat of the phase change material}} \times 100\% \quad \text{Equation 1}$$

177 3. RESULTS and DISCUSSION

178 3.1 Characterisation of the rice husk char and particles

179 The RHC used was analysed for its proximate and elemental composition, as shown in Table 1. It
 180 contains 4.47 wt% water, 1.41 wt% volatile matter, 28.49 wt% ash and 65.63 wt% non-volatile
 181 organic matter as fix carbon, as received. The elemental analysis is reported on a dry basis. Along
 182 with the 29.82 wt% of ash, the char is composed of 53.58 wt% of carbon, 2.93 wt% of hydrogen,
 183 1.57 wt% of nitrogen and 12.10 wt% of oxygen.

184 Table 1. Proximate and elemental analysis of the rice husk char

Proximate*, wt%		Elemental, wt%, dry basis	
Moisture	4.47	Carbon	53.58
Volatile	1.41	Hydrogen	2.93
Fixed carbon	65.63	Nitrogen	1.57
Ash	28.49	Oxygen**	12.10
		Ash	29.82

*as received; **by difference.

185

186 Thermogravimetric analysis in the presence of the nitrogen gas is shown in Fig. 1a. Water loss
187 appears at a temperature lower than 100 °C, suggesting moisture has been adsorbed. After the
188 water desorption, the RHC remains virtually stable with little weight loss at temperatures up to ~
189 300 °C. Results from the thermal analysis shows sufficiently stable for the application as an
190 additive in plasters, for example.

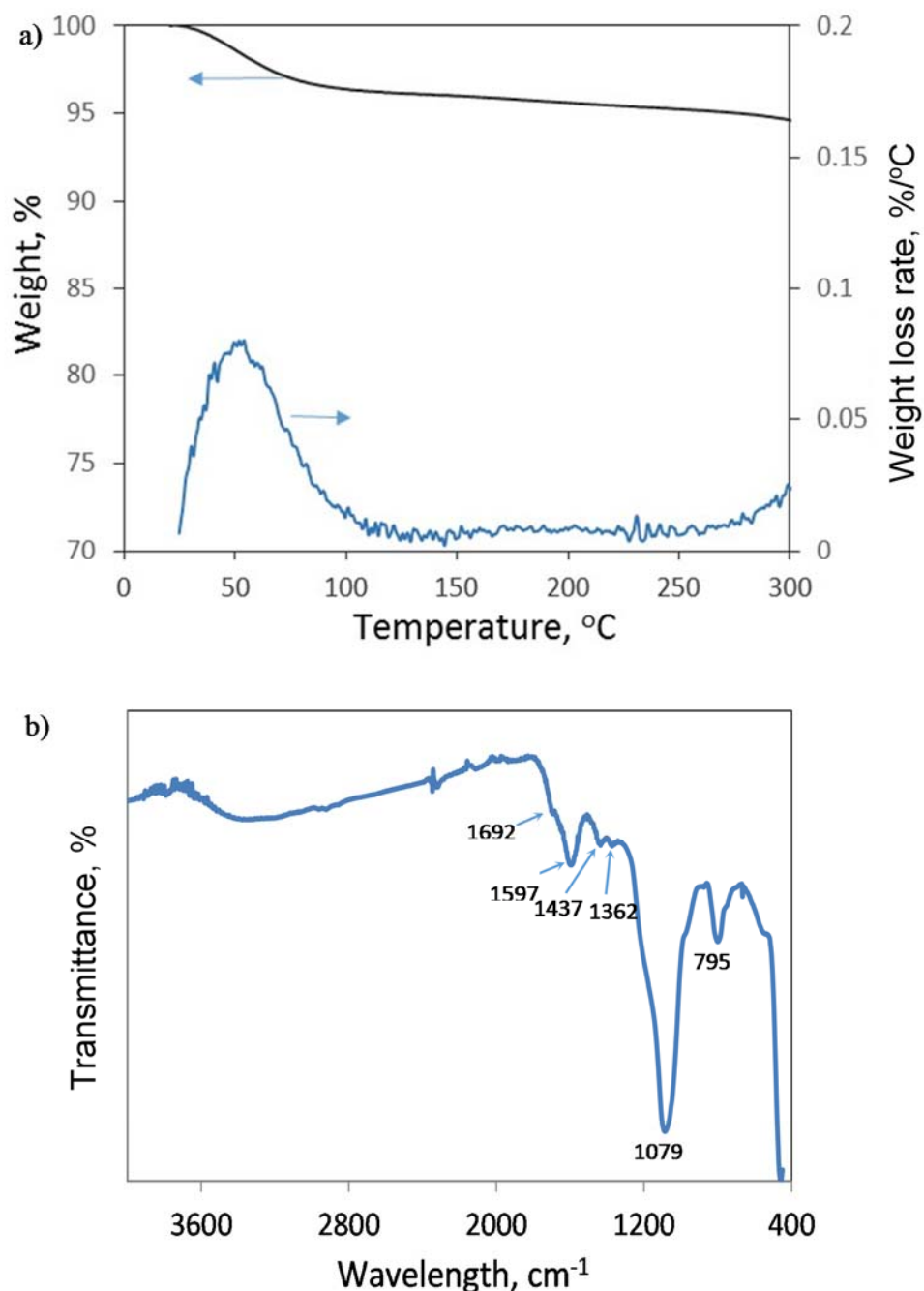
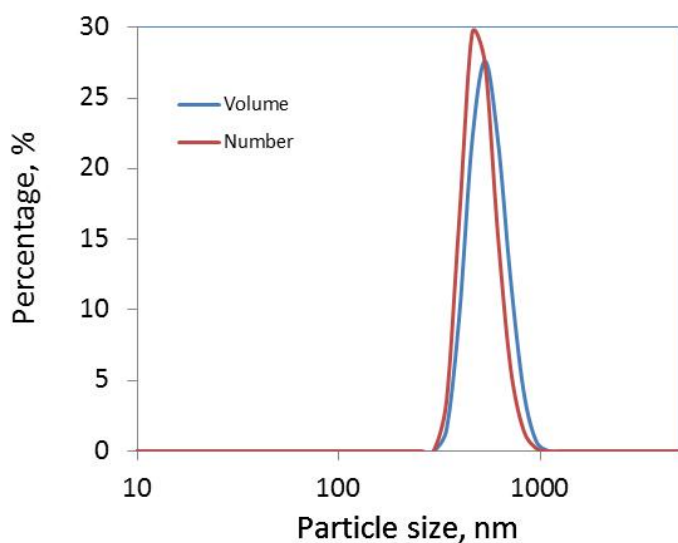


Fig. 1. (a) Thermal gravimetric analysis of the rice husk char heated at 10 K min⁻¹ in air; (b) ATR-FTIR spectroscopy of the rice husk char.

191

192 The ATR-FTIR spectrum showed the combined absorption of inorganic and organic components
193 in Fig. 1b. The strong absorption bands at 795 cm^{-1} and 1079 cm^{-1} could be assigned to (Si-O)
194 bending and stretching vibrations respectively [38-40]. This proves the existence of silica in the
195 RHC sample. The bands in the range $\sim 1400\text{-}1700\text{ cm}^{-1}$ are assignable to $\nu(\text{C}=\text{C})$ absorptions.
196 Skeletal C=C vibrations in aromatic rings could generate absorption bands at 1597 and 1437 cm^{-1}
197 [41]. The bands at 1362 and 1692 cm^{-1} can be allocated to $\delta(\text{O-H})$ and $\nu(\text{C}=\text{O})$ vibrations. The
198 existence of these aromatic carbon and oxygen-containing functional groups together with silica
199 may generate a well-balanced hydrophilic and hydrophobic surface, which can be wetted to both
200 oil and water. This demonstrates its suitability as a solid emulsifier.

201 The RHC sample was received with sizes in the range of $300\text{-}500\text{ }\mu\text{m}$. The sample was subjected
202 to ball milling using ZrO_2 milling balls of 1 mm . After grinding at 6000 rpm for 5 minutes, a well-
203 pulverised sample was obtained. The sample was dispersed in deionised water and analysed by
204 laser scattering for the size distribution and surface zeta potential. The size distribution, Fig. 2,
205 shows a size distribution centred at 576 nm (zeta average size). The zeta potential measurement
206 presented negative surface charge at -45 mV .



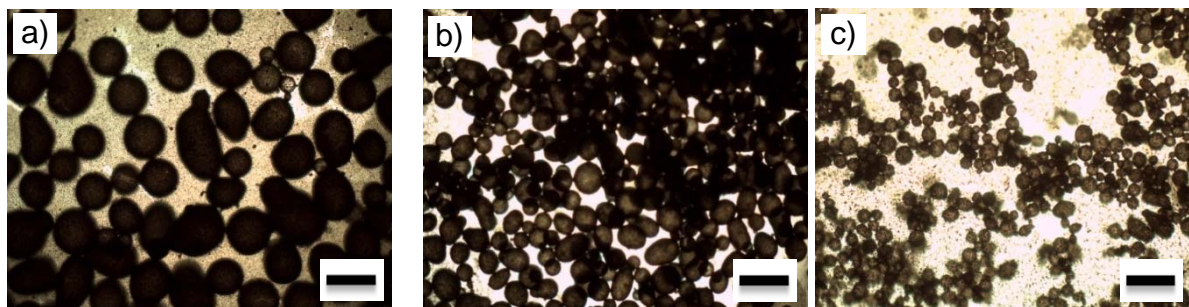
207
208 Fig. 2. Size distribution of the RHC particles measured by laser scattering.

209
210

211 3.2 Emulsification

212 The emulsification step aimed to break the phase change material into droplets with desired sizes,
213 and to facilitate the adsorption of the RHC particles on the droplet surface to form a closely packed
214 shell. These two objectives can be achieved by controlling the rotational speed of the rotor-stator
215 homogenisation tool, volume ratio of the dispersed and continuous phases and the RHC particle

216 size and concentration. In order to test the feasibility of the RHC particles as emulsifier, 3.0 ml of
217 its aqueous suspension at 1.0 wt% were emulsified with 1.0 ml hexadecane at 15,000 rpm for 2
218 minutes. The emulsion droplets formed are displayed in Fig. 3a. The black spherical and round
219 shapes are individual hexadecane droplets in the size range 50-100 μm . The droplets are well
220 covered by RHC particles. These droplets creamed to the top of the emulsion and showed good
221 stability while standing. This experimental phenomenon show RHC particles have the desired
222 wettability to both oil and water for the stabilisation of the emulsion droplets.



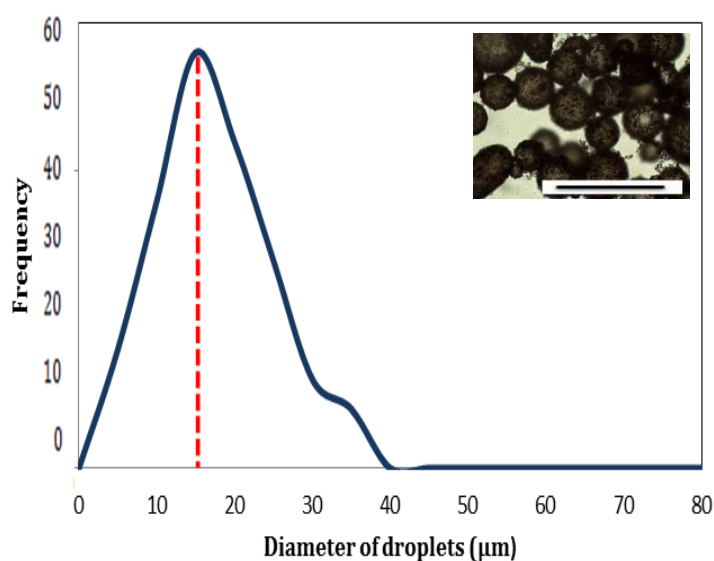
223
224 Fig. 3. Optical micrographs of hexadecane droplets in water stabilised by the rice husk char
225 particles: a) 1.0 ml hexadecane in 3.0 ml of 1.0 wt% RHC, (b) 1.0 ml hexadecane in 3.0 ml of 2.0
226 wt% RHC and c) 0.5 ml hexadecane in 3 ml of 2.0 wt% RHC suspension. Homogenised at 15k
227 rpm for 2 minutes. The scale bar denotes 100 μm .

228
229 Comparatively, another emulsion was prepared under the same condition with the RHC particle
230 concentration in water being increased to 2.0 wt% (as shown in Figure 3b). The diameter of the
231 black-coloured droplets decreases to $\sim 30 \mu\text{m}$. From this it is obvious that higher particle
232 concentration produced smaller droplets due to faster adsorption onto the droplet surface. The
233 images in Fig. 3 show the existence of surplus free particles.

234 With a char concentration of 2.0 wt%, the oil to aqueous phase ratio was decreased to 0.5 ml/3 ml
235 in order to examine the effect of phase volume ratio on the droplet formation. The droplet
236 appearances can be seen in Fig. 3c. At a low volume ratio of 0.5 ml/3.0 ml, the oil droplets become
237 significantly smaller to approximately 10 μm . Observations showed good coverage of RHC
238 particles on the droplets and appear more translucent due to the smaller size, demonstrating the
239 monolayer adsorption mechanism for RHC particles.

240 Hexadecane has a melting point at 18.7 $^{\circ}\text{C}$, viscosity close to 3 mPas and solubility in water at
241 $6.0 \times 10^{-3} \text{ g}/100\text{g}$ water at 20 $^{\circ}\text{C}$. Its droplets in a complex emulsion environment will encounter
242 stability challenges similar to that seen in miniemulsion polymerisation [42]. In the mini-emulsion
243 polymerisation, monomers in droplets tend to escape into the continuous phase during

244 polymerisation. A hydrophobic agent is added in the monomer phase to increasing the osmosis
245 pressure inside the droplet. This characteristic can effectively avoid monomers escaping into the
246 continuous phase. This strategy can be used here. Sunflower oil as a hydrophobic agent was added
247 into hexadecane at 1.0 wt%. Such oil phase of 0.5 ml was homogenised in 3.0 ml of the RHC
248 particle suspension of 2.0 wt% at 10k rpm for 5 minutes. The emulsion prepared is shown in Figure
249 4. A slower homogenisation speed of 10k rpm and a longer time of 5 minutes were used to obtain
250 more uniform droplets with a better surface coverage. The emulsion droplets prepared look robust,
251 covered well by the RHC particles in the desired size range of 10 – 30 μm , as shown in the inset,
252 for interior wall applications [5,6]. The emulsion droplets were then subjected to encapsulation.
253

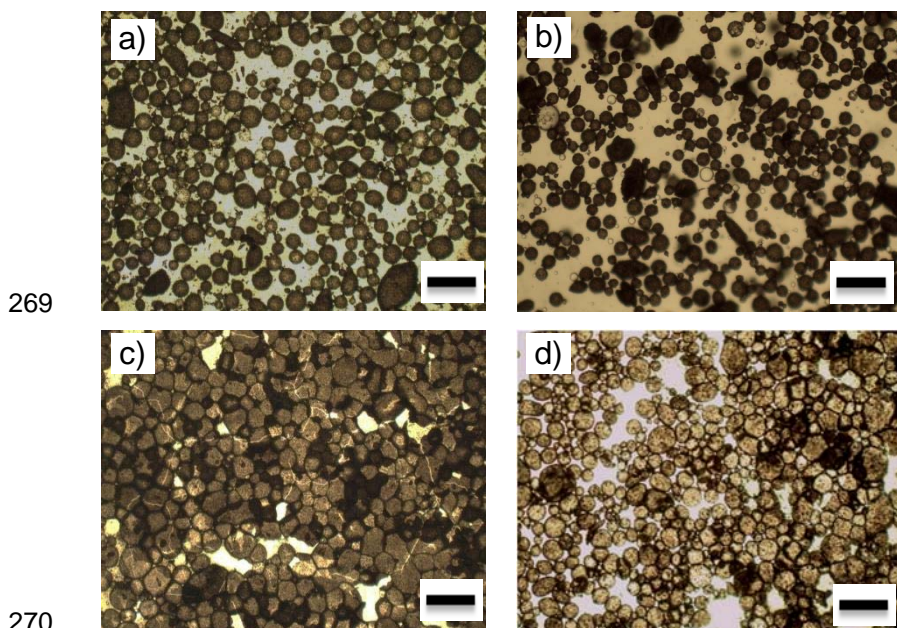


254
255 Fig. 4. Size distribution of the hexadecane droplets. Prepared from 0.5 ml hexadecane (including
256 1.0 wt% of sunflower oil) and 3.0 ml of 2.0 wt% aqueous RHC particle suspension at the rotational
257 speed of 10k rpm for 5 minutes. Inset shows the droplets with the scale bar denoting 100 μm .

258
259 **3.3 Encapsulation by layer-by-layer assembly**

260 The encapsulation was carried out by alternative adsorption of positively charged polymer
261 PDADMAC and negatively charged PSS. The RHC is negatively charged on the surface and has
262 a zeta potential of -45 mV. Due to this negative charge, the positively charged polymer
263 PDADMAC was used for the first layer of adsorptive coating. The effect of PDADMAC
264 concentration on the coating was examined using aqueous solutions at 2.0 and 5.0 wt%. On mixing
265 the emulsion mixture with PDADMAC solution, the free RHC particles flocculated. This led to
266 particle sedimentation with time. The microcapsules produced after being gently stirred for 24

267 hours were sampled from the top layer of the mixture for microscopic examination. Images are
268 shown in Fig. 5 a and b.

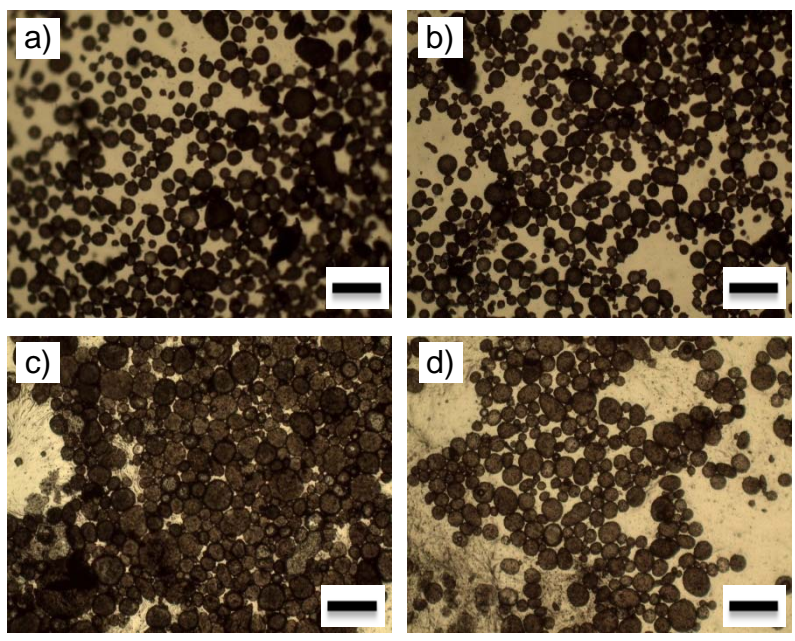


271 Fig. 5. Optical micrographs of the microcapsules coated by 2.0 wt% PDADMAC (a. wet; c dried)
272 and 5.0 wt% PDADMAC (b. wet; d. dried). The scale bar denotes 100 μm .

273

274 Both samples show microcapsules in the similar size range to their precursor emulsion. Close
275 observation confirms that the microcapsules coated by 5.0 wt% PDADMAC are structurally more
276 intact compared to that coated by 2.0 wt% PDADMAC. The microcapsules were also closely
277 examined after the water vaporisation. The microcapsules coated with 2.0 wt% PDADMAC
278 showed clear cracks and deformation due to aggregation, Fig. 5c. In contrast, the microcapsules
279 coated with 5.0 wt% PDADMAC did not rupture upon drying and remained as whole
280 microcapsules, Fig. 5d. The 5.0 wt% PDADMAC coated sample, therefore, was coated further by
281 the negatively charged PSS, and then coated by PDADMAC again, forming two and three layer-
282 coated microcapsules as shown in Fig. 6 a and c, respectively.

283 The two- and three-layer coated microcapsules remained similar in size range to their precursor
284 emulsion. The capsules had undamaged shells when suspended in water (Fig. 6 a and c), and after
285 drying (Fig. 6 b and d). It was observed that most of the three-layer coated microcapsules settled
286 at the bottom of the vial. This indicated that the three-layer coated microcapsules became heavier
287 than water, which may be due to leaching of hexadecane. On the other hand, the microcapsule
288 shell remained undamaged, indicating the shell is relatively stable.



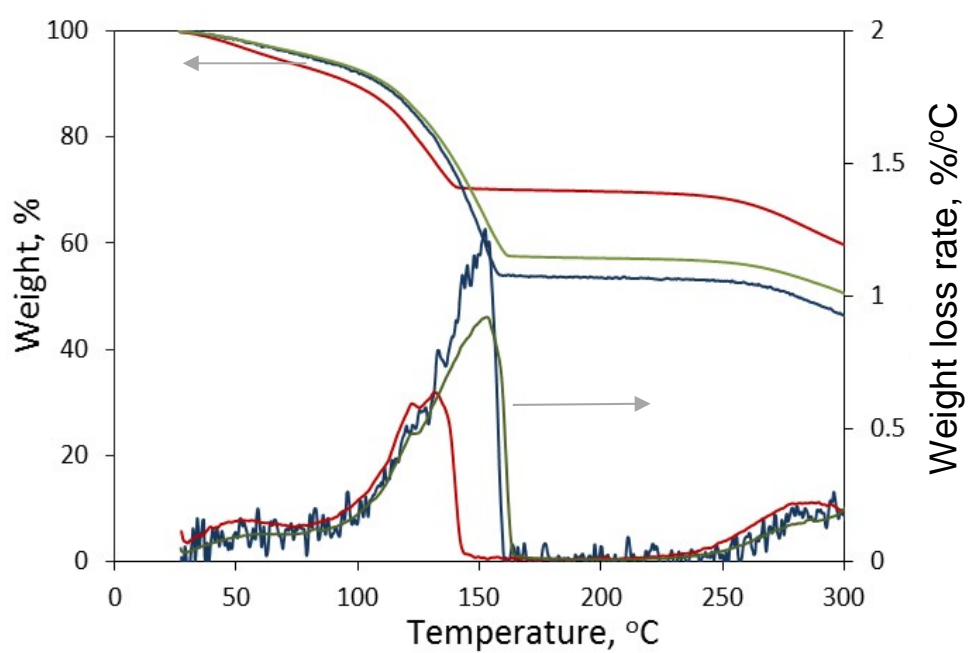
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290

291 Fig. 6. Optical micrographs of the PDADMAL/PSS-coated microcapsules: a) wet; c) dried and
 292 PDADMAL/PSS/PDADMAL coated microcapsules: b) wet; d) dried. The scale bar denotes 100
 293 μm.
 294

295 **3.4 Thermal analysis of the microcapsules**

296 The thermal stability of the microcapsules was assessed using the TGA and DSC. Results from
 297 TGA are shown in Fig. 7.



298

299 Fig. 7. Thermogravimetric analysis of microcapsules: (blue) PDADMAL-coated, (green)
 300 PDADMAL/PSS-coated, (red) PDADMAL/PSS/PDADMAL-coated.

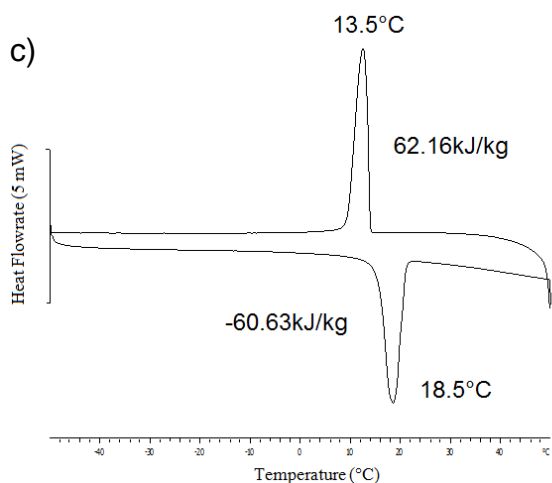
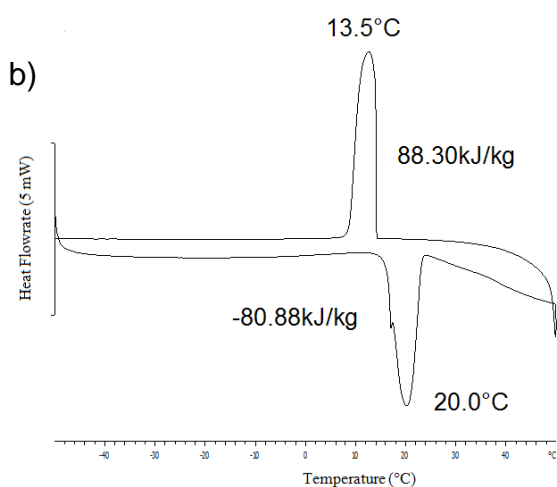
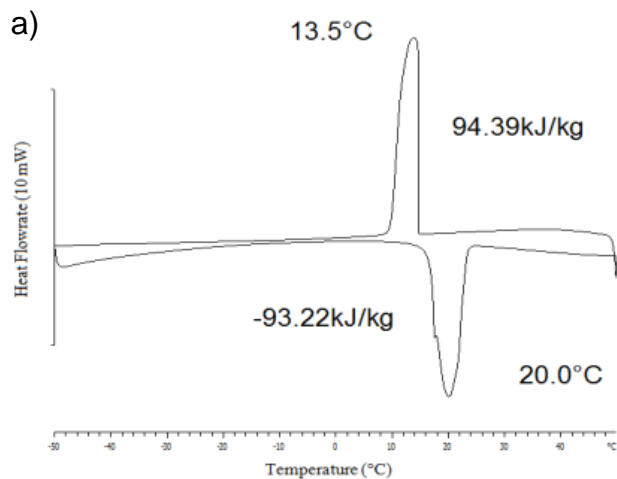
301 The test was carried out in the presence of flowing N₂ gas. The weight loss profile shows a moisture
 302 loss ~5 wt% before 75°C when microcapsules were naturally dried. This temperature is
 303 distinguished by the inflection point of the weight loss rate. The weight loss between 75 and 165°C
 304 can be assigned to hexadecane. This temperature range is significantly lower than the boiling point
 305 of hexadecane at 286.5°C, probably due to the existence of trace oxygen in the carrier gas (N₂) and
 306 the flash temperature of hexadecane (93°C). The sample weight remained virtually constant
 307 between 165 - 250°C, showing stability of the RHC particle and coating polymers in this
 308 temperature range. Both the RHC and coating polymers started to decompose at temperature over
 309 250°C as proved in Fig. 1 as well as studies into polymer degradation and stability [43]. The
 310 weight loss of the three samples are summarised in Table 2.

311 Table 2. Thermal analysis results of RHC microcapsules

SAMPLE	Weight loss, wt% by TGA			Melting Heat (kJ kg ⁻¹)	PCM, wt % by DSC
	75°C	75- 165°C	165 - 400°C		
One layer	4.25	41.77	21.22	-93.22	41.03
Two layers	4.04	38.16	19.17	-80.88	35.60
Three layers	6.33	23.54	22.56	-60.63	26.69

312
 313 Weight loss in the temperature range of 75°C to 165°C showed decreased hexadecane
 314 encapsulation ratio from 41.77 to 23.54 wt% as the number of polymer coating layers increased.
 315 Theoretical calculation illustrates that the hexadecane encapsulation ratio is controlled by the size
 316 ratio of the nanoparticles and microcapsules. The smaller the size ratio, the higher the
 317 encapsulation ratio can be. The highest hexadecane encapsulation ratio measured was 41.77 wt%,
 318 this reflects the size ratio of the nanoparticles and microcapsules. However this is lower than
 319 theoretically calculated values. The leaching of hexadecane is accountable for the lower
 320 encapsulation ratio. As discussed earlier, higher encapsulation ratios i.e. 65 wt% can be achieved
 321 when smaller size ratio is used [28].

322 The microcapsule samples were analysed by DSC (Fig. 8). The heat intake and release profiles
 323 show the melting temperatures of the three samples are close to that of hexadecane at ~20 °C,
 324 while the solidification temperatures shift to 13.5 °C, which is significantly lower than the 18°C
 325 melting point. The melting and crystallisation enthalpies of RHC microcapsules decreased as the
 326 number of polymer layers increased. One-layer coated RHC microcapsules released a latent heat
 327 of 93.22 kJ/kg, equivalent to the inclusion of hexadecane at 41.0 wt%. The two-layer coated
 328 released 80.88 kJ/kg (120 kJ/L), corresponding to 35.60 wt% of hexadecane, and the three layer



332 Fig. 8. DSC thermographs of microcapsules coated with a) one layer, b) two layers and c) three
 333 layers of polymers. Heat rate 10 K min⁻¹.
 334 coated released 60.63 kJ/kg of heat corresponding to an inclusion of 26.69 wt% hexadecane. The
 335 encapsulation ratios matched well with the weight loss measured TGA. The significant decrease
 336 in the inclusion of hexadecane could be caused by the osmosis pressure of the continuous phase
 337 that is generated by the high polymer concentration. The osmosis pressure withdraws the

338 hexadecane into the continuous aqueous phase outside. This osmosis-driven leach could be
339 overcome by controlling the relative population of the polymer chains in the continuous phase
340 and/or by adding more osmosis agent in the disperse phase. Such kind of control has been
341 successfully achieved in mini emulsion polymerisation, and also applied in our on-going work
342 with significant higher encapsulation results.

343
344 The phase change microcapsules prepared in this study were designed in the size range of 10-30
345 μm for civil engineering applications in stagnant conditions. Our ongoing research is to develop
346 phase change microcapsule slurries as working fluids for thermal energy recovery and storage. In
347 slurries, the microcapsule shell forms thermal conductive network structures to enhance heat
348 transfer and the phase change core plays an important role in increasing the heat density. To fulfil
349 the heat storage capacity of the phase change material encapsulated, the heat transfer across the
350 shell to the centre of the core (phase change material inside) needs to be achieved within the contact
351 time while recovering or releasing heat. The heat transfer rate is determined by the overall heat
352 transfer resistance, which is the sum of those from the shell and core of microcapsules. When the
353 shell is more thermally conductive, the heat transfer resistance from the core will play a
354 determining role. In order to formulate phase change microcapsule slurries with both high heat
355 transfer rate and high heat density, factors such as thermal conductivities of the shell and core, size
356 and shape of microcapsules need to be carefully designed. Simulation work has been carried out
357 to assist our design of bespoke phase change microcapsules slurries.

358 **4. CONCLUSIONS**

359 This research combines carbon capture from biomass processing and utilisation for energy storage
360 through carbon-based phase change microcapsules. The development of carbon-based phase
361 change microcapsules aims to achieve higher thermal conductivity. The carbon material used, rice-
362 husk-char, was a by-product in bio-oil production of rice husk. A phase change material,
363 hexadecane, has been successfully encapsulated with desired sizes by using the rice husk char
364 particles via emulsification. The rice husk char particles were fixed on the surface of the
365 microcapsules by polymer chains adsorbed through layer-by-layer assembly. The microcapsules
366 produced were analysed through DSC and TGA, it was revealed that one- and two-layer polymer
367 coated microcapsules accommodated ~ 41.0 and 35.6 wt% of hexadecane respectively,
368 corresponding to phase change enthalpies of 93.2 and 80.9 kJ/kg (120MJ/m^3).

369

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371

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